PROCEEDINGS

OF

THE PHYSICAL SOCIETY

OF LONDON.

MAY 1886.

I. *Experimental Error in Calorimetric Work. By* SPENCER UMFREVILLE PICKERING, *M.A., Professor of Chemistry at Bedford College**.

THE determination of the heat of dissolution of a solid in water is an operation which will always occupy a most important position in the majority of calorimetric determinations; and it is therefore desirable to ascertain what the experimental error involved in this process is, and in what direction we must look for a reduction of this error. The large number of these determinations which I have had occasion to make during the last two years will give the means requisite for an investigation of this error.

The *modus operandi* in the experiments was as follows:—The given salt was weighed out into test-tubes on feet, which were placed in an open metal beaker carefully guarded from radiation and draughts by screens; in this was suspended a delicate thermometer, a companion instrument to that used in the calorimeter itself, the exact difference in the readings

* Read February 13, 1886.

between the two instruments being known throughout the extent of their scales.

It was found that one hour * was a sufficient interval to allow for the salt to assume the temperature of the surrounding atmosphere, provided this latter remained constant during this time. In order to diminish the error in measuring the rate of cooling (or heating) during the dissolution of the salt, the temperature of the air was always maintained as nearly as possible at the temperature of the calorimetric water, the difference in the majority of cases not exceeding ·1° C., or at the most ·2° C. The correction to be applied, owing to the temperature of the salt not being exactly the same as that of the calorimetric water, was thus rendered very small, and in most cases quite negligible.

The alteration in the temperature of the salt during its removal to the calorimeter can scarcely be appreciable, since this operation does not take more than ten or fifteen seconds.

The calorimeter employed was an open calorimeter similar to that devised by Berthelot (*Mécanique Chimique*, vol. i. p. 140); a pounder such as Berthelot uses to crush salts which cake (*ibid.* vol. i. p. 183) being employed in all cases, not only as a pounder, but also as a stirrer, and the platinum vessel in which the operations were performed being always used without its cover ; indeed, free circulation of air round the calorimeter is most important in all delicate determinations. It was found that an annular cardboard disk, covering in a most imperfect manner the space between the calorimeter and the surrounding water-jacket, enclosed the air to an extent sufficient to make it act as so much calorimetric water, and introduced a very appreciable error into the results.

In dissolving an anhydrous salt, when caking generally occurs, the calorimeter proper cannot be placed on the cork tripod as in other cases, but must be supported on a cork disk covered with cardboard ; and, inasmuch as this disk was found to absorb an appreciable amount of heat from the calorimeter,

* A hygroscopic substance may be left in a tube well closed with an india-rubber stopper for two or three hours with safety; but a longer exposure should be avoided, as moisture is gradually absorbed from the air permeating the stopper.

the quantity thus absorbed had to be determined by performing a series of experiments in which a reaction of known calorimetric value was effected in the calorimeter when supported on the tripod and on the disk alternately. The use of this disk unfortunately introduces a small experimental error, since from continual pounding the form of the bottom of the platinum vessel is altered, and consequently this vessel may not be in such intimate contact with the disk at one time as at another, and the amount of heat absorbed by the latter will therefore not always be the same. The error thus introduced, however, cannot be very large, since the disk was never found to be equivalent to more than one hundredth of the contents of the calorimeter.

It was thought possible that an error might also arise in the following manner. Before the introduction of any salt into the calorimeter, all the parts of the apparatus are at the same temperature; but as soon as a reaction takes place, involving, say, the evolution of heat, the radiation from the calorimeter will raise the temperature of the vessel which is interposed between it and the water-jacket (owing to its great bulk the water-jacket itself remains practically unaltered in temperature). During the rest of the time allowed for the experiment this vessel will therefore be at a higher temperature than it was initially; and consequently the rate of cooling during the last intervals will be less than during the first one, the correction to be applied for cooling will be under-estimated, the intermediate vessel having in reality acted as so much calorimetric water. In order to ascertain whether the error from this source attained appreciable dimensions, four experiments with potassium sulphate were performed; in two of these the intermediate vessel was present as usual, while in the other two it was dispensed with. The results obtained were as follows:—

A. With the intermediate vessel:—

$$\left.\begin{array}{l}1.\ \ldots\ldots\ -7215 \text{ calories} \\ 2.\ \ldots\ldots\ -7181 \quad\ ,,\end{array}\right\}\text{Mean} \quad -7198 \text{ cal.}$$

B. Without the intermediate vessel:—

$$\left.\begin{array}{l}1.\ \ldots\ldots\ -7157 \text{ calories} \\ 2.\ \ldots\ldots\ -7185 \quad\ ,,\end{array}\right\}\text{Mean} \quad -7171 \text{ cal.}$$

Showing that the use of the intermediate vessel had no appreciable effect on the results obtained *. Where, however, large heat-disturbances take place in the calorimeter, it is safer to dispense with it entirely; and indeed the employment of it is in no case attended by any advantage.

The time required to complete the dissolution of the salt varied, of course, in different cases, but rarely exceeded 5 minutes. The loss (or gain) of heat by radiation &c. during this interval was determined separately in each experiment. It was found that with the apparatus employed, and with a difference between the temperature of the calorimetric liquid and that of the surrounding air not exceeding 2°·5 C., the rate of cooling was practically constant throughout the 20–30 minutes (and even for a considerably longer period) during which the experiment lasted; whereas for accurate measurements it was never safe to trust to the results of one experiment to determine the rate of cooling in another experiment, even though the two were performed within 10 minutes of each other, and apparently under exactly similar conditions To determine the rate of cooling, therefore, all the operations (pounding, stirring, &c.), performed during the first 5 minutes to effect the dissolution of the salt, were imitated as nearly as possible during a second, third, and sometimes even fourth and fifth similar intervals, the temperature being read at the end of each interval. The actual rate of cooling (or heating) rarely exceeded 0°·04 C. for 5 minutes, and was generally much less.

In these experiments the proportion of salt to water taken was 1 : 400 molecules†, the actual volume of the latter being about 600 cub. centim. The chief salts operated on were the sulphates of sodium, potassium, lithium, copper, magnesium, potassium-magnesium, and potassium-copper, both hydrated and anhydrous.

The thermometers were all read by estimation by means of a lens to the twentieth part of the marked divisions, *i. e.* to 0·05 millim.‡; and one such estimation-figure, being equi-

* If otherwise, the results of A would be smaller than those of B.

† With double salts 1 : 800; but, for the sake of comparison, these are here reduced so as to be comparable with the other experiments.

‡ The divisions in some of the instruments measured rather more than

valent to ·002° C., makes a difference of about 16 cal. in the molecular heat of dissolution. I should not put the estimation-figure at less than one tenth of the marked divisions were it not that these experiments afford ample proof that some reliance can be placed on smaller amounts than this.

The heat-disturbance in the calorimeter varied between *nil* and 2°·3 C., the average being rather less than 1° C.

Out of some 600 determinations of this nature, I may discard the first hundred as consisting chiefly of preliminary and imperfectly conducted experiments; the next century of determinations was also found to give an experimental error decidedly higher than the rest; these also I have therefore omitted, and will confine myself to the remaining 400 experiments. Out of these, however, it will only be the ones which were performed in duplicate which will be available for the present purposes.

Now the average difference between two such duplicate experiments, performed on the same day and with one thermometer only in the calorimeter, was found to be 26·6 calories (deduced from 76 separate experiments), giving a probable error in each experiment of $\pm$13·3 cal.; this corresponds to an error in the thermometric column of considerably less than $\pm$·05 millim.; and as the results involve not only four or five readings of the thermometer, but also the correct reproduction of every action performed in dissolving the salt during the intervals allowed for the determination of the rate of cooling, the correct determination of the salt temperature, and many other points where serious experimental error may occur, I consider that I am fully justified in concluding that the thermometers can be read to ·05 millim., and that even a certain amount of reliance can be placed on such estimation figures.

1 millim., namely 1·2 millim.; but, provided sufficient attention be paid to a certain proportion between the breadth of the mercurial column and the distance between the divisions, there is no appreciable difference between estimating the fractional portions of these two quantities. Besides practice, and uniformity in the lines themselves, nothing conduces so much to accuracy in estimation as a just proportion between the breadth of the mercurial column and the distance between the divisions. I find the best proportion to be 1 : 10; 1 : 15 is too great, and 1 : 5 too small. Different ratios, however, might suit different observers.

Where the duplicate experiments were not performed on the same day, the error was found to be greater than in the previous case; on an average, deduced from such experiments, it amounted to $\pm 19{\cdot}6$ cal. This number is, however, somewhat bigger than it should be for strict comparison with the previous one; for the experiments which yielded it belonged chiefly to the earlier ones amongst the 400 under consideration, and an increase of accuracy appeared to be made with increased practice throughout the whole series.

In what follows I deal with those duplicate experiments which were performed consecutively only. We thus have so far:—

I. Difference of two experiments where one thermometer was employed, 26·6 cal.

Now in a large number of cases two thermometers were used in the calorimeter at the same time; from these was deduced,

II. Difference of two experiments where two thermometers were employed, taking the results obtained with the same instrument in the two experiments, 41·9 cal. (from 72 experiments).

Subtracting I. from II., we get

III. 15·3 cal. as the increase of difference in two experiments due to the increased difficulty of manipulation when two thermometers are used instead of one.

IV. Difference in two experiments when two thermometers are used, comparing the results obtained with the one instrument in the one experiment with those of the other instrument in the other experiment, 53·02 cal. (from 76 experiments).

V. Difference in the results obtained from the two different thermometers in the *same* experiment, 33·95 cal. (from 142 experiments).

Now, subtracting II. from IV., we get

VI. That portion of the difference in the results given by two thermometers in any single experiment which is due to the instruments not being absolutely concordant, 11·12 cal.

(This amount will represent the sum of the errors in the calibration and standardization of the instruments. As it is dependent on two readings of each instrument, the amount attributable to each reading will be 3·7 cal., corresponding to ·014 millim., or 0·00056° C.)

Subtracting this amount from V. gives

VII. Difference due to the error inherent in reading the two thermometers, 22·83 cal., and therefore a difference due to error in reading each thermometer of 11·42 cal.

Subtracting these two quantities from I. and II. respectively, and halving the results, we obtain :—

A. In a single experiment where one thermometer is used:—

(1) Error of reading	±5·71 cal.*
(2) Error due to manipulation ...	±7·59 „
Total	±13·3 „

B. In a single experiment where two thermometers are used:—

(1) Error of reading	±11·42 cal.
(2) Error due to manipulation ..	± 9·53 „
Total	±20·95 „

These duplicate experiments being performed at exactly the same temperature, no difference will appear between them due to errors of calibration or standardization ; but in regarding the absolute value of the numbers deduced from them, this source of error must also be taken into account. The amount of this error has already been shown to be 11·12 cal. when the results of two instruments are compared (VI.) ; the total error, therefore, in experiments where one thermometer is used will have to be increased by half this amount, thus becoming ±18·86 cal. This number, then, represents the probable divergence from the truth of any one experiment ; and, from the manner in which the various thermometers were standardized (by comparison with each other), this error will probably be as great when two experiments performed at different temperatures are compared, whether they were performed with the same or with different instruments.

Perhaps, for the purpose of determining this probable error, the calculations ought to be based on the difference between duplicate experiments performed *not* on the same day, in which case the error would be somewhat larger. I have not done so, however, chiefly owing to uncertainty in the number

* Corresponding to ·021 millim. of the mercurial column.

given for this quantity (see above). Many causes also which tend to increase the difference when the experiments are not performed consecutively might not apply in general. Amongst these I may mention the very hygroscopic nature of many of the salts taken, where a difference in the state of moisture of the atmosphere would affect the extent to which traces of water were absorbed during their exposure while being transferred to the weighing-tubes: these substances, again, were often kept in sealed tubes containing sufficient for two or three determinations only, and the contents of the various tubes may not have been dried to precisely the same degree.

II. *On Delicate Calorimetric Thermometers. By* SPENCER UMFREVILLE PICKERING, *M.A., Professor of Chemistry at Bedford College**.

IN the foregoing communication it has been shown that the average error of a determination of the heat of dissolution of a salt in $400H_2O$ amounts to $\pm$ 18·86 cal.; but this is only an *average*, and it must not be overlooked that the error in some cases may exceed this very considerably. It is not uncommon to find a difference of 40 or 50 cal. between two duplicate experiments (although the average error in such cases is only $\pm$13·3 cal.), and a proportionately larger error must therefore be expected occasionally in the comparison of two experiments at different temperatures.

The determinations from which these conclusions were drawn consisted of a series of experiments with various salts at temperatures ranging from 1° to 26° C., where it was imperative that the greatest possible accuracy should be attained, and also that the experiments at the different temperatures should all be strictly comparable with each other. The thermometers employed had a range of 15° C., and a total length of 600 millim.; it was therefore impossible to increase their length sufficiently to make one instrument embrace the whole range of 25° C., and any increase in the delicacy (by increasing the size of the bulb) would have involved a diminution in their range, so that more than two instruments would have

* Read February 13, 1886.

been required, while in such experiments it is obviously of the greatest importance that as few instruments as possible should be used.

With a view to overcoming these difficulties the following expedient was adopted, whereby the delicacy of the instrument was increased six- or sevenfold, its range was made to embrace that of all temperatures at which a mercurial thermometer can be used, and its registration was rendered (for these purposes) practically independent of calibration and standardization error.

The principle on which it was worked consisted in removing a portion of the mercury, by the application of heat, into the upper chamber, and thus adjusting any particular point in the instrument so as to register any required temperature. Experiments on the same substance at different temperatures were thus made absolutely comparable, exactly the same portion of the scale being used in each case.

The zero point of the thermometer being thus altered for each experiment, the actual temperature in degrees Centigrade which it registers will not be known with any great degree of accuracy; but this is not necessary in calorimetric work: the heat of chemical combination is affected to such a small extent by temperature, that an error of ·05° or ·1° C. in this will be unimportant; and by a rough comparison of the thermometer with some standard instrument after each adjustment of the mercury, the temperature which it registers can be easily ascertained within ·01° or ·02° C.

This thermometer (No. 62839) possessed a total length of 746 millim., of which 565 millim. constituted the divided portion of the stem, each division being 1 millim., and ten such divisions being termed 1 degree. The bulb measured 72 millim. in length, and was made out of glass cylinder instead of being blown, a detail which is rarely attended to in the construction of delicate thermometers, but one which is most important in giving the bulb greater stability and greater uniformity of action. The weight of mercury in the bulb was 36·23* grams,

* In the other instruments, with a range of 15° C., the weight of mercury varied between 13·6 and 15·6 grams; the bore of the tube of No. 62839 would be considerably more than twice as fine as in these. Fuller details respecting these instruments will be found in the Phil. Mag. March 1886.

and the total range of the instrument only 3°·4 C., giving 166 millim. to each degree C.; one estimation figure (·05 millim.) would therefore represent ·0003° C.

In using this thermometer it is first suspended in the calorimeter containing water at a temperature a certain known degree above that at which the experiments are to be made; a very small flame is then applied to a point just below the upper chamber (which in such instruments must be of considerable size), by which means the column of mercury is broken off at the part thus heated, and the separated portion remains in the upper chamber, the tube being much too fine to permit of it being shaken down again. After cooling it is put into a bath at the required temperature, and compared with some standard instrument. In this way the registration of the thermometer can be adjusted to any required temperature within ·05° C. without the least difficulty; but greater accuracy could be obtained if necessary.

This thermometer was employed in a large number of experiments, and the general results, as will be shown below, proved to be satisfactory. But it possessed one serious imperfection, or, more properly speaking, its delicacy brought into light an imperfection which must be inherent, although it has hitherto been unnoticed in all mercurial thermometers.

As is well known, the bulb of a thermometer does not expand regularly when heated ; "en effet," to quote Berthelot's words, "la marche de l'instrument est intermittent, c'est-à-dire que le niveau n'est souvent atteint qu'après une série de petites oscillations" *. To obtain a state of equilibrium the

* *Méc. Chim.* i. p. 178. It is curious to note that even while Berthelot is warning his readers against this source of error he appears to have fallen into it himself. On p. 163 he gives the results of a comparison of two thermometers placed in a bath of water, the temperature of which was rising, and read simultaneously at intervals of ten minutes; from this and other closely concordant comparisons he finds 6·702 degrees of the one instrument are equivalent to 14·827 of the other; but, on looking more closely at each reading, it will be found that

(1)	a rise of	0°·9	in the one	corresponds	to a rise of	1°·1	in the other.
(2)	„	0·7	„	„	„	2·2	„
(3)	„	0·6	„	„	„	1·5	„
(4)	„	1·1	„	„	„	0·9	„
(5)	„	1·2	„	„	„	1·1	„

Vastly discordant numbers.

thermometer must be tapped on the top with the finger, or some such means adopted to overcome the inertia of the bulb before each reading. The larger the bulb and the finer the bore of the tube, the more apparent does this inertia become: with instruments such as the less delicate ones here mentioned a dozen or less taps are sufficient to overcome it, but with No. 62839 it was found that continuous tapping for two or three minutes was absolutely necessary. The extent to which error from this source may accumulate may be drawn from the fact that this instrument, when the mercury is *rising* to the temperature of the bath in which it is placed, will register 6 millim. lower than when *falling* to the same temperature, however long it be left in the bath, if it be not tapped (the temperature of the bath in this case was such that the mercury stood at about the middle point of the stem). Again, it was found, by means of a series of experiments in which the height of the column was read when the instrument was inclined at different angles, that with thermometer 55082, which possessed a blown bulb containing 15·6 grams of mercury, a difference of 6·6 millim. in the reading was made when the instrument was placed horizontally instead of vertically; making due allowance for the greater size of the bulb and greater fineness of the bore in 62839, this latter instrument would probably exhibit a difference of at least ten times this quantity under similar treatment. This will give some adequate idea of how great an effect the expansion of the bulb under pressure may have on the reading.

Now, besides the inertia of the bulb, which may be overcome by a sufficient amount of tapping, there appears to be another and more serious imperfection, due to what may be termed a permanent alteration in size, as opposed to the other, which may be called temporary, and one which no amount of tapping will overcome. It would seem that the bulb of this, and every thermometer, has two different shapes, one when the column is rising, the other when it is falling. The following simple experiments will serve to show this.

The thermometer being suspended in the calorimeter full of water, the contents of this were heated or cooled slightly, and the rate of cooling (or heating) determined during consecutive intervals.

In the first column the time is entered, in the second the reading of the instrument, and in the third the rate of cooling or heating.

A. Experiments in which a rate of *heating* was determined.

I.

Time.	Reading (arbitrary).	Rate.
0	-1°	
Hot water added.		
1 min.	19·96	
		·11
4 "	20·07	
		·095
7 "	20·165	
		·08
10 "	20·245	mean =·10.
		·135
13 "	20·38	
		·09
16 "	20·47	

II.

Time.	Reading.	Rate.
0	-5°	
Hot water added.		
2 min.	20·685	
		·075
5 "	20·76	
		·095
8 "	20·855	
		·085 mean ·09.
11 "	20·94	
		·09
14 "	21·03	

In this case the rate of heating is constant from the very beginning: during the first three minutes it differs from the mean of the other intervals by +·01 in Exp. 1 and by —·015 in Exp. 2, both of these quantities being well within the limits of experimental error.

III.

Time.	Reading.	Rate.
0	54°	
Cold water added.		
2 min.	20·555	
		·005
5 "	20·56	
		·09
8 "	20·65	
		·085 mean ·093.
11 "	20·735	
		·105
14 "	20·84	

IV.

Time.	Reading.	Rate.	
0	54°		
Cold water added.			
2 min.	19·45		
5 „	19·465	·015	
8 „	19·555	·09	mean ·103.
11 „	19·645	·09	
14 „	19·775	·13	

In these two experiments, however, this is not so; the rate of heating (as registered) during the first interval is almost *nil*, in each case exactly ·088 less than the mean deduced from the other intervals. Thus, when the column of mercury rises to any temperature it will go on rising regularly afterwards, indicating the rate of heating correctly, but when it *falls* to that temperature a certain time elapses before it will begin to rise afterwards; although the mercury must be expanding during this interval, the column is stationary, and therefore the bulb must be expanding, and assuming a new form.

The following experiments are complementary to the preceding ones and illustrate the same fact.

B. Experiments in which a rate of *cooling* was measured.

I.

Time.	Reading.	Rate.	
0	55°		
Cold water added.			
3 min.	22·16		
6 „	21·76	·41	
9 „	21·41	·34	mean ·39.
12 „	20·99	·42	
15 „	20·59	·40	

II.

Time.	Reading.	Rate.	
0	53°		
Cold water added.			
3 min.	22·21		
6 „	21·84	·37	
9 „	21·48	·37	mean ·342.
12 „	21·155	·325	
15 „	20·815	·34	

The difference between the rate of cooling measured during the first interval and that during the remaining ones being +·02 in the one experiment, and +·028 in the other, *i. e.* practically *nil.*

III.

Time.	Reading.	Rate.
0	0	
Hot water added.	°	
2 min.	20·65	·20
5 „	20·45	·36
8 „	20·09	·30 mean ·34.
11 „	19·79	·37
14 „	19·42	

IV.

Time.	Reading.	Rate.
0	-3°	
Hot water added.		
1 min.	25·58	·22
4 „	25·36	·425
7 „	24·935	·415 mean ·40.
10 „	24·52	·36
13 „	24·16	

The difference between the first and remaining intervals being −·14 and −·18 in the two experiments. Thus whichever be the direction of the motion of the mercury it will continue in that direction, giving correct results, but, if the direction be changed, an interval elapses before the motion becomes apparent, and a considerable error will be introduced.

The above are but typical experiments out of a large number performed, and all of which gave the same results; indeed, every determination of the heat of dissolution of a salt afforded a fresh exemplification of the fact.

Of course the alteration in the size of the bulb will invalidate any experiment unless its effect be counteracted. This was always done in every experiment by taking care that, if a rate of cooling was to be measured after the salt had been dissolved, the liquid should be cooling also before its introduction, and *vice versâ*; the motion of the mercury, and therefore the shape of the bulb, being the same at the beginning and end of the experiment, no error would occur. In

such an experiment, where for instance a rate of cooling obtained, and the salt dissolved with absorption of heat, no period of inertia in the column would occur; but if the salt dissolved with evolution of heat, two such periods would occur, and, though this would not affect the accuracy of the results, a certain time would elapse before the apparent rate of cooling became constant, extending often to three intervals of 3 or 5 minutes each (for the whole of these intervals cannot be spent in tapping the thermometer as in the experiments quoted above, but are chiefly occupied in reproducing the actions performed in effecting the dissolution of the salt), thus creating a serious increase in the duration of an experiment. This was obviated by removing the thermometer from the calorimeter, touching the bulb with some warm object, when, on replacing it, the column fell to the temperature of the calorimeter, and proceeded to give the rate of cooling at once; where a rate of heating was to be determined, the thermometer was cooled (by evaporation from the surface) instead of heated. As a few millim. rise or fall are sufficient for the purpose, the heating or cooling of the contents of the calorimeter in such an operation is quite negligible *.

The change of size in the bulb, as deduced from the experiments already quoted, is, perhaps, somewhat exaggerated, owing to an under-estimation at the time of the amount of tapping which was necessary to overcome the temporary inertia of the bulb. The following, even more simple, experiments are free from such an error, and bring to light other facts concerning this phenomenon.

The method of procedure here consisted in suspending the thermometer in a calorimeter containing a much larger volume of water than the one generally used, taking the instrument out, heating and cooling it alternately, when, on its being replaced, readings of the same temperature were obtained, the column having fallen or risen to that temperature respectively.

As it was found to be impossible to keep the temperature of the bath constant during the requisite time, any observed

* The water-equivalent of the immersed portion of this thermometer was 2·09 grams, that of the calorimeter and contents about 610 grams. A heating of the former sufficient to produce a rise of 5 mm. would raise the temperature of the latter only 0·0001° C.

reading, say when the column was rising to the temperature, was compared with a theoretical reading consisting of the mean of the previous and subsequent readings, both of which were obtained when the column was falling to the temperature. The differences here quoted will represent the total difference between the readings with rising and falling columns. After the thermometer had been replaced in the bath, it was tapped continuously and read at intervals of one minute till it became quite stationary; between five and seven such readings were made in the series here given, although it will be necessary to quote the final reading only in each case. An interval of about 8 minutes elapsed between these final readings, all the intervals in each separate series being exactly equal.

I.

	Registered.	Theory.	Difference.
	°	°	
Immersed after being heated 10°	14·08		
,, ,, cooled 10	14·08	14·103	−·023
,, ,, heated 10	14·125	14·118	+·097
,, ,, cooled 10	14·155	14·185	−·030
,, ,, heated 30	14·245	14·233	+·012
,, ,, cooled 10	14·310	14·313	−·003
,, ,, heated 10	14·380		
		Mean	·015

II.

	Registered.	Theory.	Difference.
	°	°	
Immersed after being cooled 10°	26·83		
,, ,, heated 10	26·86	26·845	+·015
,, ,, cooled 10	26·86	26·908	−·048
,, ,, heated 10	26·955	26·918	+·037
,, ,, cooled 10	26·975	27·008	−·033
,, ,, heated 10	27·06	27·038	+·022
,, ,, cooled 20	27·10	27·123	−·023
,, ,, heated 20	27·185	27·175	+·010
,, ,, cooled 10	27·25		
		Mean	·027

III.

	Registered.	Theory.	Difference.
	°	°	
Immersed after being heated 10°	45·845		
,, ,, cooled 10	45·755	45·804	−·049
,, ,, heated 10	45·763	45·718	+·045
,, ,, cooled 10	45·680	45·717	−·063
,, ,, heated 10	45·670	45·643	+·027
,, ,, cooled 10	45·605	45·655	−·045
,, ,, heated 10	45·640	45·595	+·045
,, ,, cooled 10	45·585	45·635	−·050
,, ,, heated 10	45·630		
		Mean	·046

Without exception, therefore, a reading when the thermometer is falling to a given temperature is higher than when it is rising to this same temperature, and the difference between these two readings appears to be independent of the extent of the foregoing fall or rise; a fact which will be shown more clearly in a series of similar experiments with another thermometer to be quoted below. The difference in the two readings, however, is considerably influenced by the position of the mercury in the stem; from these experiments it would appear to be directly proportional to the height of the column, the total difference in each case being $\frac{1}{1000}$ of this height.

Although this difference is very appreciable, it must be remembered that it corresponds to a difference of very small dimensions in the capacity of the bulb. The 0°·015 measured in the first series is equivalent to 0°·0009 C., and represents but 0·0000004 c.c., or but little over one millionth part of the total capacity of the bulb (2·64 c.c.), a quantity so small that there is no wonder in its having hitherto escaped observation. The considerable force necessary to push a column of mercury through a long very fine tube is, I should say, quite sufficient to account for this expansion of the bulb; it is well illustrated by the fact that a quick fall of but a small amount causes the mercury to separate at the neck of the bulb.

The question now arises whether this instrument, possessing such serious imperfections, is really workable, or whether we have not pushed thermometric delicacy beyond the limits compatible with accuracy.

The various determinations of the heat of dissolution of salts which were made with this thermometer give the means of answering this question.

As shown in the previous communication, $\pm$13·3 cal. is the average error of each experiment when compared with a duplicate one performed under the same conditions; of this 7·59 cal. are error due to manipulation and 5·71 cal. to error of reading. The manipulation-error will be independent of the thermometer employed, but the reading-error will be smaller in direct proportion to the delicacy of the instrument. As an estimation-figure with No. 62839 represents about $\frac{1}{6\cdot4}$ of what it does in the case of the instruments to which these numbers refer, the reading-error with it ought to be only $\frac{5\cdot71}{6\cdot4}$,

or about ·9 cal., giving a total error for each experiment of $\pm(\cdot 9+7\cdot 59=)8\cdot 49$.

Now the average difference of two duplicate experiments with this thermometer was found to be 14·84 cal. (deduced from 38 experiments), giving an error of only $\pm 7\cdot 42$ * cal. for each experiment, a quantity even smaller than that which would have been anticipated, proving conclusively that such an instrument can be worked with just as much certainty as the less delicate ones. The fact that the total error here is even less than the manipulation-error alone in the other experiments is due to greater care being taken in manipulation, a larger number of intervals being allowed for the determination of the rate of cooling. It must be remembered, however, that this diminution of the difference between two duplicate experiments by no means represents the total advantages accruing from the use of this thermometer, for, the same portion of the instrument being used for experiments with the same substance at all the different temperatures, these will be on the same footing as duplicate experiments themselves. We shall, therefore, have to make no addition to this error when comparing different experiments in a series, and we thus get rid at once of the additional error of $\pm 5\cdot 56$ cal., which had to be admitted with the other instruments †.

The extra time required for experiments with such an instrument is considerable ; the determination itself occupies two or three times as long as with an ordinary thermometer, and the preliminary adjustment of the mercury ‡ and the

* I am probably very much overstating the error here ; this number is deduced from *all* the experiments in which this thermometer was used. Several of these were performed before the peculiarities of the instrument were thoroughly known, and contained known sources of error ; eliminating these, the average error of the remaining experiments (24 in number) is only $\pm 3\cdot 33$ cal., a surprisingly small quantity.

† From what has been mentioned in the Phil. Mag. March 1886 as to the error of standardizing this thermometer, the divergence of any measurement from the absolute value will probably not be more than ·00045° C. for each degree C. measured, or ± 3–4 cal.

‡ In one instrument which I possess a small particle of dust has become fixed in the tube just below the upper chamber, the result of which is that the column of mercury, whenever it has passed a few millimetres beyond this point, breaks off there and shoots up into the upper chamber.

comparison with a standard occupies the greater part of an hour. It is possible to do three determinations at different temperatures with it in a day; but this means a very hard day's work, and could only be effected after much practice.

Although the results obtained with this thermometer may appear satisfactory as measured by the average error, they still leave much to be desired. It is impossible to feel absolute confidence in an instrument which possesses such serious imperfections; and, apart from this, I was desirous of investigating the matter further for its own sake, and producing an instrument in which delicacy did not involve the sacrifice even of convenience.

It occurred to me that the substitution of a double bulb for the single bulb of No. 62839 would probably result in a considerable increase in strength under pressure. Such an instrument, therefore, I had constructed. Considerable difficulty was met with in boiling the mercury in a double bulb thoroughly, but this was overcome in a masterful manner, while at the same time the other parts of the instrument were so perfect that I believe it is the finest thermometer of its kind ever constructed, in this country at any rate. The stem was of the required stoutness, and the bore, while being flat, was well rounded at the edges, thus exposing no crevices into which the mercury would find it difficult to enter, as is usually the case with flat bores, and as was so with No. 62839. The length of each bulb of this instrument, No. 63616, was 55 mm., the total weight of mercury in them being 30·5 grams, considerably less therefore than in the other thermometer and less than double that in the bulbs of some of the less delicate thermometers. The scale was rather less open than in 62839, the total range of 60 cm. representing 3°·85 C., or 154·3 mm. to each degree, one estimation-figure representing therefore $\frac{1}{3000}^{\circ}$.

The results of two series of experiments with this instrument similar to those with 62839, last described, gave the following results :—

If it were possible to introduce such an obstacle at will, the time expended in separating the mercury by heat, and the danger thereby incurred, would be obviated. I am not without hopes of succeeding in effecting this.

I.

	Registered.	Theory.	Difference.
	°	°	
Immersed after being cooled 1°	45·69		
,, ,, heated 1	45·765	45·688	+·077
,, ,, cooled 1	45·685	45·790	−·105
,, ,, heated 1	45·815	45·703	+·112
,, ,, cooled 10	45·720	45·733	−·113
,, ,, heated 10	45·850	45·768	+·082
,, ,, cooled 10	45·815	45·899	−·084
,, ,, heated 10	45·947		
		Mean	·096

II.

	Registered.	Theory.	Difference.
	°	°	
Immersed after being heated 10°	13·985		
,, ,, cooled 10	13·95	14·00	−·05
,, ,, heated 10	14·015	13·93	+·085
,, ,, cooled 10	13·91	14·029	−·119
,, ,, heated 10	14·043	13·933	+·110
,, ,, cooled 10	13·955	14·044	−·089
,, ,, heated 10	14·045		
		Mean	·091

Thus, contrary to expectation, this instrument not only shows a difference in reading when the column is rising or falling to any temperature, but that difference is even greater, and considerably so, than with No. 62839. This is certainly remarkable, and tends to show that a full explanation of this difference has not yet been obtained, for the double bulb would undoubtedly possess a greater rigidity than the single bulb of the other instrument; although the combined length of the two bulbs is 110 millim. as opposed to 72 millim., the diameter of the tubing of which they were made was considerably less, 4·83 millim. instead of 6·86 millim. (internal measurements), and the wall of the tubing also was considerably stouter, 0·76 millim. instead of 0·635 millim., and a small improvement in these last two items would cause a very considerable increase in the rigidity. Another peculiarity in this instrument is that the difference in the readings is independent of the height of the column of mercury; or at any rate very nearly so.

Series I. of the above experiments affords good proof that the difference in readings is independent of the distance through which the column has fallen or risen; the mean difference of the first three numbers in the last column being

·098, and that of the last three ·093; numbers practically identical, although the fall or rise was 1 degree in the former, and 10 degrees in the latter.

Although this difference, due to what I have termed the permanent alteration in the size of the bulb, is greater with 63616 than with 62839, it is otherwise with the temporary alteration. An experiment similar to the above, but the tapping of the instrument being omitted, gave a difference of 0°·23 in the mercury standing at 45·8, whereas with 62839 it amounted to 0°·6 (at 27°); these numbers representing the sum of the permanent and temporary alterations, the latter only will be represented by (·23 − ·096 =) 0°·13, and (·6 − ·027 =) 0°·57 in the two instruments respectively. This tends to confirm an opinion expressed by Mr. Casella, that a considerable portion of this temporary alteration is due, not to the bulb, but to the mercury not entirely filling the bore of tube of its own accord, owing to the extreme flatness of this latter at the edges. The tube of which 63616 was made presented no such imperfections. However, neither the permanent nor temporary difference can be in any degree attributed to the action of the tube in this latter instrument, but is wholly due to the bulb itself; for the thermometer was first made up with a small bulb*, containing only 3 grams of mercury, in which state it showed no difference whatever in the readings obtained under different conditions, with or without tapping. The comparative smallness of this temporary alteration in the case of 63616 renders this instrument far more convenient and satisfactory than the other. Instead of requiring two or three minutes continuous tapping in order to obtain a correct reading, less than one minute is sufficient, and this must very materially increase accuracy in calorimetric determinations. I have not as yet used this thermometer in a sufficient number of experiments to ascertain the experi-

* Where the bulb is to contain as much as 20 or 30 grams of mercury, it is well to have the instrument made up temporarily with a small bulb, for the purpose of calibration, as with fine tubes some rough handling is often necessary to pass a short thread of mercury along them.

It would appear that 30 grams of mercury is not an uncommon amount in the instruments used by Berthelot (*Méc. Chim.* i. 165), although they are far less delicate than those described in the present communication. He even refers to thermometers containing 250 grams! (p. 156).

mental error with it; but the uniformity of its action and the increased concordance of the rate of cooling registered in successive intervals, leads me to feel confident that the error with it will be considerably less than with 62839.

From what has already been said as to the smallness of the reading-error in this instrument, it may be stated that we have pushed thermometric delicacy quite as far as is desirable with regard to calorimetric work, and that to produce a further degree of accuracy in this branch of study, the methods employed, and not the thermometers, must be improved.

In conclusion, I wish to take this opportunity of expressing my warmest thanks to Mr. Casella and to his assistants for the scientific interest which they have shown in this investigation, and the ungrudging manner in which they have spared no pains to help me in attaining my object.

III. *The Relations of Pressure, Temperature, and Volume in Saturated Vapours.* *By* W. C. Unwin, *M. Inst. C.E.**

In the interesting and laborious paper of Messrs. Ramsay and Young, there are given four relations of a simple kind between the pressures, temperatures, and volumes of saturated vapours and the heat of vaporization of a number of substances. These relations are not given as exact relations, but as suggestive of laws approximately satisfied by very different substances over a very wide range of conditions.

Now long ago Hirn pointed out that, as for saturated vapours there exists only a single value of p and t corresponding to one specific volume v, there must be a direct relation between t and v, and between p and v, independent of p or t. But hitherto no exact relation has been found, and we remain still in the condition of being obliged in every thermodynamical calculation to fall back at every step on data either interpolated from tables of experimental values, or determined by the aid of purely empirical formulæ. Nor is this all: the formulæ are themselves cumbrous and are not interrelated.

Regnault's formula, giving p in terms of t for instance,

* Read February 27, 1886.

cannot be inverted to get t in terms of p, though in practical calculations the pressure is almost always the given datum. Further, if differentiated to obtain $\frac{dp}{dt}$ an expression is obtained far too cumbrous for ordinary use. Rankine's formula is nearly as accurate, and is both simpler and gives an inverse function; but the expression for $\frac{dp}{dt}$ is cumbrous. The expression for latent heat is necessarily independent, but then the density or specific volume ought to be expressed in terms of the formulæ for latent heat and pressure and temperature. But there being no simple expression for $\frac{dp}{dt}$ it is more common to resort to the quite independent empirical formula of Zeuner.

For purely scientific purposes no absolute difficulty or inaccuracy is caused, and no advance can be hoped for till rational expressions are found. When such expressions are found, also, it may probably prove, as Hirn surmises, that they will not have the simplicity which some people expect in all natural laws. The practical difficulty, again, can be surmounted by means of the tabulated values of p, t, $\frac{dp}{dt}$, calculated with great care and labour by Prof. Zeuner and Prof. Cotterill. Nevertheless the author thinks that some clearness would be introduced into the teaching of thermodynamics, and possibly some facility gained in practical calculations, if only amongst empirical expressions to which recourse must be had, one could be found accurate enough and yet so simple that all the related functions could be derived from it. The paper of Messrs. Ramsay and Young suggested an attempt in that direction.

It might be expected that the approximate relations stated by Profs. Ramsay and Young could be deduced from some of the empirical relations already established. This, however, is not strictly the case.

It is known for instance that the expression

$$p = AT^{5 \cdot 5},$$

where A is a constant and T is reckoned from an arbitrary

zero, approximately satisfies the law connecting the pressure and temperature of saturated vapours.

Differentiating,

$$\frac{dp}{dT} = 5{\cdot}5 A T^{4{\cdot}5};$$

so that

$$T \frac{dp}{dT} = 5{\cdot}5 A T^{5{\cdot}5} = 5{\cdot}5 p.$$

Consequently

$$\frac{T}{p} \frac{dp}{dT} = 5{\cdot}5:$$

a relation which should be approximately satisfied for different vapours.

Thus, for instance, reckoning from the zeros given below we get from the values of $\frac{dp}{dt}$ in Messrs. Ramsay and Young's tables the following values of $\frac{T}{p}\frac{dp}{dt}$:—

Substance ...	Bisulph. of Carbon.	Ethyl Alcohol.	Water.	Mercury.
Zero (Above −273°C)	144°.	208°.	210°.	322°.
Pressure in mm.				
100	5·913	5·323	5·183	5·243
500	5·749	5·616	5·794	5·598
1000	5·666	5·802	5·808	5·707
5000	5·201	5·540	5·645	......
10,000	......	5·429	5·503	......
20,000	......	5·291	5·302	......

At first sight it looks as if this were similar to the relation $t\frac{dp}{dt}$ = constant at any one pressure, given in Messrs. Ramsay and Young's paper. But, obviously, it is a quite different relation from the difference in the reckoning of temperature. It is, besides, a purely empirical relation, and the constancy of the values obtained may serve as a useful warning against accepting such correspondence of formula and data as indicating that the formula expresses a real law.

The principal relation discussed by Messrs. Ramsay and Young is that

$$t \frac{dp}{dt}$$

is constant for different vapours at the same pressure. In their table (Proc. Phys. Soc. vol. vii. p. 301*) values of this quantity, very carefully and laboriously calculated, are given for various vapours at pressures ranging from 10 to 20,000 mm. of mercury. It will easily be seen that the numbers in each horizontal line in their table approximate to constancy, varying in extreme cases by possibly 30 per cent.

If now these numbers are divided by the pressures so as to form values of

$$\frac{t}{p}\frac{dp}{dt},$$

the constancy of the horizontal lines of figures will remain unaffected, while the vertical columns will approach to constancy almost as nearly as the horizontal columns. The following table gives these values, with some of those for mercury corrected and with those for vapour of carbonic anhydride added:—

Values of $\frac{t}{p}\frac{dp}{dt}$ for different vapours.

Pressure in millims.	Carbon bisulphide, CS_2.	Ethyl bromide, C_2H_5Br.	Ether, $C_4H_{10}O$.	Chloroform, $CHCl_3$.	Mercury, Hg.	Sulphur, S.	Water, H_2O.	Ethyl alcohol, C_2H_5OH.	Carbonic anhydride, CO_2.
100	12·80	13·64	13·04	......	......	......	16·07	16·42	......
500	10·83	11·31	11·22	11·66	13·20	12·12	13·81	14·39	......
1000	10·10	10·37	10·51	10·85	11·89	11·20	12·95	13·83	......
3000	8·68	8·96	9·24	9·27	11·23	9·67	11·58	11·99	......
5000	8·22	8·26	8·66	8·46	9·73	......	10·89	11·29	......
10,000	......	......	......	......	......	......	10·03	10·39	7·62
15,000	......	......	......	......	......	......	9·50	9·89	7·63
20,000	......	......	......	......	......	......	9·13	9·54	7·57
50,000	......	......	......	......	......	......	......	......	6·77

But now it may be pointed out that $\frac{t}{p}\frac{dp}{dt}$ is not a mere arbitrary expression for

$$\frac{t}{p}\frac{dp}{dt}=\frac{r}{Apu}$$

(Hirn, tom. i. p. 319). That is, it is the ratio between the

* Phil. Mag. vol. xx. p. 526 (December 1885).

total heat of evaporation and the heat expended in external work. What we have found, therefore, is that this ratio approaches constancy for widely different substances and under considerable differences of pressure. This approximation to constancy appears to me to lie at the basis of all the relations Messrs. Young and Ramsay have found.

The constancy of this ratio of internal and external work, for different vapours at one pressure, has been investigated by Messrs. Young and Ramsay from other data, but it does not seem to have occurred to them that it would be obtained in the simple way given above.

The author noticed that another relation, namely,

$$\frac{t^2}{p}\frac{dp}{dt},$$

gave values for each vapour, far more constant at different pressures than

$$\frac{t}{p}\frac{dp}{dt}.$$

The following table gives some of these values:—

Values of $\frac{t^2}{p}\cdot\frac{dp}{dt}$ for different vapours.

Pressure in millims.	Carbon bisulphide, CS_2.	Ether, $C_4H_{10}O$.	Mercury, Hg.	Sulphur, S.	Water, H_2O.	Ethyl alcohol, C_2H_5OH.	Carbonic anhydride, CO_2.
100	3426	3394	7053	......	5218	5049	......
500	3324	3329	7231	8437	4995	4909	......
1000	3313	3321	7247	8275	4932	4956	......
5000	3220	3233	......	7936	4745	4610	......
10,000	......	......	......	.....	4670	4528	1889
20,000	......	......	......	......	4570	4455	1991
50,000	......	......	......	......	......	......	2018

This suggested that probably an empirical relation of this kind could be found expressing the relation of pressure and temperature very simply and with considerable accuracy.

Let, for instance, for steam the values of $\frac{t^{2\cdot25}}{p}\frac{dp}{dt}$ be formed. We get:—

t.	p.	$\frac{t^{2\cdot25}}{p}\frac{dp}{dt}$.
273	4·60	21660
298	23·55	21970
323	91·98	22020
348	288·5	21940
373	760·0	21870
398	1743·9	21830
423	3581·2	21790
448	6717·4	21770
473	11689·0	21950

Where the greatest and least values differ from the mean by only 0·7 per cent. But the expression, the values of which have been found, is integrable. Putting $n+1$ for the index of t, we get for a general approximate relation between the pressure and temperature of vapours,

$$\log_e p = \alpha - \frac{\beta}{t^n}. \qquad (1)$$

From this are easily derived the following equations, in which for convenience the logarithms are common logarithms.

$$\log p = a - \frac{b}{t^n} \qquad (2)$$

$$t = \left(\frac{b}{a-\log p}\right)^{\frac{1}{n}}. \qquad (2\,a)$$

$$\frac{1}{p}\frac{dp}{dt} = 2\cdot3025\,\frac{nb}{t^{n+1}}. \qquad (3)$$

$$= 2\cdot3025n\,\frac{(a-\log p)^{\frac{n+1}{n}}}{b^{\frac{1}{n}}}. \qquad (3\,a)$$

$$\frac{t}{p}\frac{dp}{dt} = 2\cdot3025\,\frac{nb}{t^n} \qquad (4)$$

$$= 2\cdot3025n(a-\log p). \qquad (4\,a)$$

For the latent heat, besides the ordinary formula,

$$\mathrm{L} = m - \frac{n}{(a-\log p)^{\frac{1}{n}}}. \qquad (5)$$

And consequently if v is the volume in cubic metres of the vapour and s that of the liquid,

$$v-s=\frac{\mathrm{JL}}{t\dfrac{dp}{dt}}$$

$$=\frac{13{\cdot}497\mathrm{L}}{pn(a-\log p)}. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In all these equations the quantity required is expressed simply in terms of the pressure or the temperature, a result not obtainable with the formulæ previously used.

Formulæ for Steam.

To test the value of these equations, the author has calculated the constants for steam most suitable for the complete range of Regnault's experiments, from $-30°$ C. to $230°$ C., and from 0·4 millim. pressure to 20,000 millim. pressure. The proposal of a new empirical formula, and one not so accurate as Rankine's or Regnault's, for the relation of p and t in the case of steam, will probably appear the reverse of commendable. Still the fact that it gives a series of expressions, all directly derived from it, simple enough for ordinary use in engine calculations and accurate enough for practical purposes, is a strong reason in its favour. Its applicability can only be determined by testing its accuracy in a sufficient number of cases. In all the following calculations the calculated values are compared with the most accurate values thus far computed, over a range of pressure and temperature greater than would occur in practical cases.

The primary equation, derived from Regnault's data, for millimetres of mercury, Centigrade degrees reckoned from $-273°$ C., and common logarithms is

$$\log p=7{\cdot}5030-\frac{7579}{t^{1{\cdot}25}}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

which gives

$$t=\left(\frac{7579}{7{\cdot}5030-\log p}\right)^{\frac{4}{5}}. \quad . \quad . \quad . \quad . \quad . \quad (7a)$$

The following table gives the values of p calculated from t with Regnault's experimental values and values calculated by Rankine's formula for comparison :—

Temperature, Centigrade.	Temperature, absolute.	Pressure in millims. Regnault.	Pressure in millims. by formula.	Error in millims.	Pressure in millims. by Rankine.	Error in millims.
$-30°$	$243°$	0·386	·401	+ ·015	·35	−·036
−20	253	0·91	·982	+ ·072	·89	−·02
−10	263	2·08	2·229	+ ·149	2·07	−·01
0	273	4·60	4·709	+ ·109	4·47	−·13
5	278	6·53	6·69	+ ·16		
10	283	9·17	9·40	+ ·23	9·05	−·12
15	288	12·70	13·01	+ ·31		
20	293	17·39	17·83	+ ·44	17·33	−·06
25	298	23·55	24·07	+ ·52		
30	303	31·55	32·18	+ ·63	31·57	+·02
35	308	41·83	42·61	+ ·78		
40	313	54·91	55·72	+ ·81	55·05	+·14
45	318	71·39	72·24	+ ·85		
50	323	91·98	92·85	+ ·87	92·26	+·28
55	328	117·48	118·30	+ ·82		
60	333	148·79	149·48	+ ·69	149·15	+·36
65	338	186·94	187·50	+ ·56		
70	343	233·08	233·61	+ ·53	233·48	+·40
75	348	288·50	288·60	+ ·10		
80	353	354·62	353·59	−1·03	355·04	+·42
85	358	433·00	433·21	+ ·21		
90	363	525·39	523·48	−1·91	525·70	+·31
95	368	633·69	633·72	+ ·03		
100	373	760·00	757·35	−2·65	760·0	0
105	378	906·41	904·27	−2·14		
110	383	1075·4	1071·5	−3·9	1074·8	−·6
115	388	1269·4	1263·3	−6·1		
120	393	1491·3	1485·6	−5·7	1490·1	−1·2
125	398	1743·9	1735·4	−8·48		
130	403	2030·3	2020·2	−10·1	2028·0	−2·3
135	408	2353·7	2347·5	− 6·2		
140	413	2717·6	2710·2	− 7·4	2713·8	−3·8
145	418	3125·6	3114·6	−11·0		
150	423	3581·2	3564·5	−16·7	3575·5	−5·7
155	428	4088·6	4064·4	−24·2		
160	433	4651·6	4633·4	−18·2	4643·6	−8·0
165	438	5274·5	5262·6	−12·9		
170	443	5961·7	5941·6	−20·1	5951·2	−10·5
175	448	6717·4	6694·2	−23·2		
200	473	11689·0	11665·4	−23·6	11675·0	−14·0
230	503	20926·0	20951·7	+25·7	20945·0	+19·0

The following short table gives some values of t calculated from p :—

p.	t.	
	Calculated by (7a).	Observed.
4·60	272·7	273
91·98	322·8	323
760·00	373·2	373
3581·2	423·2	423
11689·0	473·1	473

The following are the derivative expressions. A few values are calculated from each and compared with the values very laboriously calculated by Zeuner from Regnault's formula.

$$\frac{1}{p}\frac{dp}{dt} = \frac{21815}{t^{2\cdot25}} \quad \ldots \ldots \quad (8)$$

$$= \frac{(7\cdot5030 - \log p)^{\frac{9}{5}}}{441\cdot3} \quad \ldots \quad (8\,a)$$

t.	$\frac{1}{p}\frac{dp}{dt}$.	
	By formula (8).	From Zeuner.
273	·07201	·0[illegible]50
323	·04932	·04979
373	·03567	·03577
423	·02688	·02685
473	·02090	·02083

$$\frac{t}{p}\frac{dp}{dt} = \frac{21815}{t^{1\cdot25}} \quad \ldots \ldots \quad (9)$$

$$= 2\cdot8782(7\cdot5030 - \log p). \quad (9\,a)$$

t.	p.	$\frac{t}{p}\frac{dp}{dt}$.		From Zeuner.
		By equation (9).	By equation (9 a).	
273	4·60	19·659	19·69	19·52
323	91·98	15·929	15·94	16·08
373	760·00	13·304	13·30	13·34
423	3581·2	11·368	11·37	11·36
473	11689·0	9·890	9·89	9·85

The latent heat of vaporization has hitherto been expressed only in terms of the temperature by the empirical formula

$$L=796{\cdot}23-0{\cdot}695t, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where t is the absolute temperature, and the smaller terms containing higher powers of t are omitted. From the relation between p and t we get

$$L=799-\frac{894}{(a-\log p)^{\frac{4}{3}}}. \quad . \quad . \quad . \quad . \quad (10\,a)$$

t.	p.	L. By equation (10).	L. By equation (10 a).	From Zeuner.
273	4·60	606·5	607·0	606·5
323	91·98	571·8	571·7	571·7
373	760·00	537·0	536·3	536·5
423	3581·2	502·3	501·0	500·8
473	11689·0	466·5	465·9	464·3

The new formula (10 a) is more accurate than the one (10) commonly used.

Let v be the volume in cubic metres of a kilogram of steam, and s the volume of the same quantity of water, usually taken at 0·001,

$$v-s=10{\cdot}821\,\frac{L}{p(a-\log p)}, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where p is still expressed in millimetres.

p.	$v-s$. By equation (11).	$v-s$. From Zeuner.
4·60	208·7	210·6
91·98	12·14	12·05
760·00	1·652	1·650
3581·2	·3833	·3839
11689·0	·1255	·1257

Other Vapours.

The following equations may be useful. That for ether agrees extremely well. The mercury equation less well; but

the errors are considerably less than those of Rankine's equation in his paper of 1850. The data are all from Regnault.

Alcohol:—

$$\log p = 7{\cdot}448 - \frac{8784}{t^{1{\cdot}29}}.$$

Ether:—

$$\log p = 6{\cdot}9968 - \frac{3047}{t^{1{\cdot}153}}$$

Mercury:—

$$\log p = 9{\cdot}8651 - \frac{597{\cdot}5}{t^{0{\cdot}69}}.$$

Carbonic acid:—

$$\log p = 8{\cdot}4625 - \frac{302{\cdot}8.}{t^{0{\cdot}77}}$$

IV. *A Map of the World on* Flamsteed's *Projection.* *By* Walter Baily, *M.A.**

[Plate I.]

In Flamsteed's *Atlas Cœlestis* the projection used is one invented by him and described in the Preface to that work as follows:—

"Conceive the globe or sphere to be compassed about with an infinite number of infinitely fine threads all exactly parallel to the equator. Let all the circles usually drawn upon the globe, as the equator, the ecliptic, the meridians, &c., be supposed drawn and divided, and let the constellations also be formed upon them, and the stars laid down in their proper places. Let also the meridian passing through the middle of any constellation be conceived drawn on the globe, and covered with a fine thread with as many of the adjacent circles as you may think convenient. Conceive the threads on which the constellation is painted to be cut off from the surface of the globe; and that which passes through the middle being extended straight on the middle of some paper or perfectly plane superficies, let the rest be placed on it at right angles to the middle meridian, but reverted."

* Read February 27, 1886.

Flamsteed used his projection only for maps of portions of the celestial sphere, and he did not apply it to the polar regions, as the distortion which would otherwise have been produced would have been inconvenient to an astronomer.

The Preface points out the advantages of the method as follows :—" So will you have the picture of the Constellation projected upon it, in which the parallels of declination will be straight lines and their distances exactly equal, the same as they are on the globe, as will also the distances and differences of the right ascensions of any two stars that are equally distant from the pole." The advantage in Geography of a map in which the parallels of latitude are equidistant straight lines parallel to the equator is obvious, as the position with regard to latitude is seen at a glance. There is, moreover, a property of this projection which is evident at once from the way in which the projection is constructed, viz. that the area of every part is preserved unaltered. The imaginary threads have simply slipped over one another, like the cards in a pack, without altering their distances, so that only a distortion of form has occurred. This property is not referred to by Flamsteed, either because he did not notice it, or because it was of no importance in Astronomy. I venture to submit, however, that in Physical Geography it is a property of considerable importance, and that it would be advisable in many physical maps to use this projection. For instance, in maps showing rainfall, depth of the sea, height of the land, ocean currents, prevailing winds, distribution of plants and animals, &c., it is essential to take account of the area occupied, and maps in which this is correctly shown could not fail to be of use. In Plate I. is shown a map of the World on Flamsteed's projection, the small square at the side representing 1,000,000 square miles on the same scale.

The formulæ for constructing the map are readily obtained. Take the equator as the axis of x, and the central meridian (say the meridian of Greenwich) for the axis of y. Let x, y be the coordinates of a point m° of longitude from the central meridian, and n° of latitude from the equator. Then if a is the length of a degree of latitude in the scale adopted,

$$y/a=n, \quad x/a=m\cos n^\circ.$$

Hence the equation to a meridian m degrees from the central meridian is

$$\frac{x}{a}=m\cos\left(\frac{y}{a}\cdot 1^\circ\right).$$

V. *Note on a "Relation between the Critical Temperatures of Bodies and their Thermal Expansions as Liquids." By* T. E. Thorpe, *Ph.D., F.R.S., and* A. W. Rücker, *M.A., F.R.S.**

A paper bearing the above title was published by us in the Journal of the Chemical Society of London for April 1884, and has recently been discussed by MM. A. Bartoli and E. Stracciati†. As these gentlemen have done us the honour to make use of a formula deduced by us from the simple expression given by Mendelejeff for the expansion of liquids, we should like to state exactly the position which we ourselves think ought to be assigned to it, and the use which may legitimately be made of it.

Prof. Mendelejeff has shown‡ that the expansion of liquids under constant pressure between 0° C. and their boiling-points may be expressed by means of the very simple formula

$$V_t=\frac{1}{1-kt};$$

where V_t is the volume at t° (that at 0° C. being unity), and k is a quantity which differs for different substances, but which may for any one substance be considered invariable between 0° C. and the neighbourhood of the boiling-point.

The great merit of Mendelejeff's law is that it is proved by him to express the law of expansion to within the limits of the differences between the results of different observers experimenting on the same liquid. Thus, if the results of any one observer alone are considered, they may no doubt be most

* Read April 10, 1886.

† *Ann. Chim. Phys.* Mars 1886, p. 384.

‡ Journ. Chem. Soc. April 1884.

accurately expressed by a formula of the type

$$V_t = 1 + a't + b't^2 + c't^3.$$

Another equally reliable observer will, however, obtain for the same liquid a formula

$$V_t = 1 + a''t + b''t^2 + c''t^3,$$

where a', b', c' differ appreciably from a'', b'', c''. These slight differences depend on the unavoidable errors of experiment, which may perhaps in the future be diminished, but which at present affect the work of the best observers using the best known methods. Hence formulæ such as those given above can only be considered as approximations to the true law of the expansion of the liquid to which they refer. That law will be most nearly given by combining the results of several physicists whose methods and observations are equally good, rather than of relying upon those of any one.

Now Mendelejeff has shown that the volumes calculated at different temperatures by means of the formula

$$V_t = \frac{1}{1-kt}$$

differ less from the results of good observers than they do from one another. It might in any given case be possible to obtain another more complex formula which would express the *mean result* more accurately, but it would remain very doubtful whether the greater mathematical accuracy obtained represented the physical facts more closely. Mendelejeff (as we think rightly) considers that the simplicity of the formula which he has suggested gives it a special claim upon our attention; and he proves that it expresses, at all events as a first but very close approximation, all *that we certainly know* about the expansion of liquids.

It is therefore no argument against Mendelejeff's formula to remark, as MM. Bartoli and Stracciati have done, that

$$V_t = \frac{1}{1-kt} = 1 + kt + k^2t^2 + k^3t^3 + \&c.;$$

and that in the formulæ given by Pierre, Kopp, Hirn, Thorpe,

&c., the constants a, b, and c do not differ by a constant ratio, as the expression would require. This criticism would only hold good if all these observers had obtained the same, or closely identical, values of a, b, and c; whereas, as a matter of fact, the values of b and c given by different observers may differ very widely. The very merit of Mendelejeff's remark is that, although the results of no one physicist are expressed by

$$V_t = 1 + kt + k^2t^2 + k^3t^3,$$

yet that this formula in its simpler form,

$$V_t = \frac{1}{1-kt},$$

expresses the results of all as accurately as those results will allow; and that since it is thus sufficiently accurate and extraordinarily simple, it may claim to be the best general formula hitherto proposed for expressing the laws of liquid expansion.

These remarks are subject to the conditions which Mendelejeff made clear, that the formula was only applied to the range of temperature between 0° and the neighbourhood of the boiling-point, and that the constant k increases slightly as the temperature rises. This latter fact indicates that the law, though very accurately expressing the known facts, is only an approximation to the truth.

Mendelejeff's formula, then, appears to us to stand in somewhat the same position as Boyle's or Charles's laws. It is a first approximation, which expresses the facts, under given conditions of temperature and pressure, with great accuracy. The difference between the two cases is that, whereas the deviation of each of the principal gases from Boyle's law has been studied, Mendelejeff has shown that the most careful researches do not enable us to state with certainty what is the magnitude of the error caused by applying his formula to any particular liquid. They show only that k increases very slightly as the temperature rises.

Having thus defined as accurately as we can the position which we think that Mendelejeff's law holds, we need hardly say that we do not claim any higher status for our own formula connecting the law of expansion and the critical temperature.

We were most careful to express in our paper our appreciation of the fact that our expression was based upon Mendelejeff's, and therefore it ranked only as a theoretical deduction from an extremely close approximation to the truth, and is to be employed only under the conditions for which that approximation was valid.

Thus we have shown that the critical temperature of a liquid (T_c) is given very approximately by the formula

$$T_c = \frac{TV - 273}{a(V_t - 1)};$$

where V_t is the volume at $t°$ C., $T = 273 + t$, and a is a constant which we proved is nearly $= 2$.

We should, however, never have thought of applying this formula to determine the critical temperature of water from the expansion up to 200° C. We have not applied it to water at all, on account of the well-known peculiarities of the expansion of that substance; but had we done so, we should have regarded it as holding only between 0° C. and the boiling-point. We have distinctly laid it down that it is under these conditions k is to be determined*. In proving, therefore, that the values of the critical temperature, calculated from the expansions at temperatures above the boiling-point, vary very widely from those obtained under the conditions adopted by Mendelejeff and ourselves, MM. Bartoli and Stracciati have only shown that the formula does not hold good under circumstances to which its authors never intended it to be applied.

We are, however, gratified to find that these gentlemen, notwithstanding their criticisms, show a reliance upon our formula even greater than that which we feel ourselves. The values of the constant a given in our paper prove that its true value is uncertain, at all events to 1 per cent. or more. MM. Bartoli and Stracciati, however, give in their second paper a number of critical temperatures calculated by the formula to tenths of a degree. If the tenth of a degree is to be determined with accuracy, the constant a must be known to 0·025 per cent.

* Journ. Chem. Soc. *loc. cit.* p. 139.

VI. *On the Cause of the Solar-Diurnal Variations of Terrestrial Magnetism.* *By* Professor Balfour Stewart, *LL.D., F.R.S.**

In attempting to account for the Solar-diurnal inequalities of Terrestrial Magnetism, scientific speculators have ranged over the whole field of likely explanations. Some of them think that they have now finally driven the truth into a corner, and are in hopes of ultimately securing the object of their pursuit.

I shall begin by enumerating the chief hypotheses which have been proposed;

(1) There is, first, that of the direct magnetic action of the Sun upon the Earth. There are, however, many serious objections to this hypothesis. One of these is the great difficulty attending the supposition that the Sun is capable of acting as a powerful magnet, since terrestrial analogies would lead us to infer that matter at the high temperature of the Sun is quite incapable of possessing magnetic properties. Again, we have strong evidence that changes in the range of the daily variation of magnetic declination lag behind corresponding solar changes in point of time. This kind of behaviour is apparently inconsistent with direct magnetic action, and points rather to some indirect influence probably caused by the radiant energy of the Sun, inasmuch as the changes and turning-points of such indirect influences due to radiation are well known to lag in respect of time behind the corresponding changes and turning-points in their cause. Finally, Dr. Lloyd and Mr. C. Chambers † have both shown that direct solar magnetic action will not account for the peculiarities of the diurnal magnetic variation. We may therefore perhaps dimiss this hypothesis.

(2) The next hypothesis which I shall introduce is that of Faraday. Reasoning from his discovery that oxygen is magnetic and becomes weaker in its power when heated, he concludes that when the Sun heats a certain portion of the Earth's atmosphere, this renders that portion less magnetic

* Read April 10, 1886.

† Proc. Royal Irish Academy, Feb. 22, 1858, and Phil. Trans. 1863.

than those other portions not subjected to solar influence. This kind of action is thus seen to be equivalent to a displacement by means of solar influence of the magnetic matter of the Earth, and hence implies a corresponding displacement of the lines of magnetic force. Now there is unquestionably truth in this hypothesis, but yet there is very great doubt whether it will account for the diurnal oscillation as we know it. It will form *a cause*, but yet it will not be *the chief cause*. It is obviously one prominent peculiarity of Faraday's hypothesis, that in it the action of the Sun must, to ensure its probability, be associated with the great mass of the Earth's atmosphere, that is to say with the lower strata as well as with the upper; or rather with the lower strata in preference to the upper, bearing in mind the superior mass of the former and their greater nearness to the magnetic Earth. Now we know both from observations of the declination and horizontal force (Proc. Roy. Soc. March 22, 1877, and Phil. Trans. 1880, p. 541) that the action of the Sun in producing diurnal variations of these elements is one and a half times as powerful at epochs of maximum as it is at epochs of minimum sun-spot frequency.

But it is very difficult, if not impossible, to imagine that the great mass of the atmosphere can be heated by the Sun one and a half times as much at epochs of maximum sun-spot frequency as it is at epochs of minimum sun-spot frequency; and yet we must imagine this if we suppose that Faraday's hypothesis accounts for the diurnal variation. Certainly the facts of meteorology are strongly against any such belief. Again, during our summer the heating influence of the Sun is considerably greater in the Northern than in the Southern Hemisphere, while during our winter the reverse will be the case. Totally apart from the diurnal variation we ought therefore, if Faraday's hypothesis be true, to find a very perceptible difference in the mean magnetic condition of the Northern Hemisphere between summer and winter, and a like difference too in the Southern Hemisphere, the one being at the same moment differently affected from the other. But there are no traces of such a phenomenon, the annual and semi-annual variations being quite of a different nature and none of them very large.

(3) Let me now discuss the hypothesis that these variations are caused by earth-currents. These currents were first detected by W. H. Barlow, and were at a later period observed and studied by C. V. Walker. They are now continuously recorded by photography at the Royal Observatory, Greenwich, and at the Central Russian Observatory.

With respect to these currents, I have always maintained that in type they bear all the marks of being secondary currents generated in the moist conducting crust of the Earth, and caused by small but abrupt changes in the magnetism of the Earth. Whether this be the true explanation or not, it is at any rate, I venture to think, consistent with what we know of electrical action. But while I should thus feel disposed to regard these phenomena as effects rather than causes, in their primary sense at least, it is manifest that, when once generated, such currents will influence the needle; and the results of the Greenwich observers induce us to think that such influence is very great and forms perhaps the chief immediate cause of those oscillations of the needle called disturbances, which are quite different from the solar diurnal variation. In one sense therefore such currents may be effects, while in another they are causes, but causes of disturbances rather than of the daily variation.

It may, however, be replied that earth-currents may be complex phenomena, and that while their most important manifestations may be due to induction, thus being primarily effects rather than causes, yet another portion of them may operate as a true cause producing the solar-diurnal variation. Now there are two objections to this hypothesis; and one of these is, that we know of no physical agency that will produce in the Earth's crust currents of this nature, which, in order to account for the solar-diurnal variation, must be one and a half times more powerful at times of maximum than at times of minimum sun-spot frequency. Another objection is that Sir George Airy has not been able to detect any resemblance in form between the regular diurnal progress of the magnet and that of the earth-currents. We think therefore that we may dismiss this hypothesis.

Now, if it be unlikely that these magnetic variations are caused either by the direct magnetic action of the Sun,

or by earth-currents, or by the heating effect of the Sun on the chief mass of the Earth's atmosphere, we seem to be driven by the method of exhaustion to look for their cause in the upper atmospheric regions. We shall, however, have to show that there is no improbability in locating their cause in these elevated regions, otherwise our method of exhaustion will have done us no service. In the first place, I need hardly say that if the cause we are in search of be in these upper regions, it must either be in the shape of a set of electrical currents, or in some other shape with which we are quite unacquainted; but the nature of this discussion precludes us from entertaining the latter supposition; and we are therefore driven to regard electrical currents as being the only conceivable cause, if this cause is to be located in the upper atmospheric regions.

I shall now attempt to reply to two imaginary objections that may be raised as to the possibility of such currents. In the first place, it may be said that while undoubtedly rarified air is a conductor of electricity, yet it is not a good conductor; and where can we look for sufficient potential to drive currents through these upper atmospheric regions? To this I would reply that *as a matter of fact* we know that there are visible electric currents in the upper atmospheric regions which occur occasionally at ordinary latitudes, and which are very frequent, if not continuous, in certain regions of the Earth. I allude to the Aurora, which is unquestionably an electric current, and must therefore influence the magnetic needle. Furthermore, both with respect to its times of occurrence and to the disposition of its beams, the Aurora manifests a close connection with the phenomena of terrestrial magnetism, occurring at ordinary latitudes only when there are great magnetic disturbances, and the disposition of its beams having a distinct reference to lines of magnetic force. We are therefore justified in asserting that there is no impossibility in conceiving a set of electrical currents, intimately associated with certain phenomena of terrestrial magnetism, to exist in the upper region of the Earth's atmosphere.

In the next place, the objection may be raised, How is it possible to suppose any cause that will make such currents

one and a half times more powerful at times of maximum than at times of minimum sun-spot frequency? Can it be imagined that the radiant energy of our luminary varies in this proportion? Now it has been remarked by Professor Stokes that an increase in the radiative power of the Sun would most probably imply, not only an increase in general radiation, but a special and predominant increase in such actinic rays as are probably absorbed in the upper regions of the Earth's atmosphere. These regions will therefore greedily absorb the new rays, their temperature will rise, and, as is known to be the case for gases, the electrical conductivity of the strata will be increased*. Thus, even if we imagine the general atmospheric current to remain constant, a greater proportion of it would be thrown at such times into those heated regions which had become good conductors; but then it is likewise probable that the current itself would be increased as well as increasingly diverted into a particular channel.

Such an explanation appears to receive support from the curious and suggestive fact that the lunar influence on the Earth's magnetism, as observed at Trevandrum, is greater during the day than during the night, and greater perhaps, too, at times of maximum than at times of minimum sun-spot frequency. If the arguments now advanced be generally assented to, we may presume that, while it is unlikely that the cause of the daily variation exists anywhere else than in the upper regions of the Earth's atmosphere, there is no objection to our imagining that it resides there in the form of a set of electric currents. Such currents will of course affect the needle directly, but they will also affect the magnetic earth, and any affection of the magnetic earth will again influence the needle. The question thus arises, To what extent do these hypothetical currents act directly upon the needle, and to what extent do they act upon it indirectly by influencing the magnetism of the Earth? That this question is not unimportant will be manifest by considering what takes place

* It seems not impossible, too, that the constitution of these strata with respect to aqueous vapour, may be different at times of maximum and at times of minimum sun-spot frequency; hence their absorbing power may be different.

when a powerful electromagnet influences a needle. In this case probably only a small portion of the influence is due to the direct action of the current, while a large portion is due to the iron of the electromagnet that has been magnetized by the current. In order to study this point it will perhaps be desirable that we limit ourselves to the solar diurnal variations of declination, as these are of a simple definite type in each hemisphere, the type in the one hemisphere being the reverse of that in the other. Let us therefore consider the peculiarities of this variation, particularly in the regions on either side of the magnetic equator.

Here we find, speaking generally, that north of the equator the extreme westerly deflection of the marked pole of the needle is reached at 2 P.M., while south of the equator this pole reaches its extreme easterly deflection at the same hour. Now, if we attempt to picture to ourselves any general change in the magnetic system of the Earth that will produce these results, it will be one of a very artificial character. On the other hand, these motions of the needle, which cannot well be explained by any easily conceivable temporary change of the Earth's magnetic system, can very easily be explained by a system of atmospheric currents. In the northern hemisphere we should have a set of positive currents flowing from the equator northwards, while in the southern we should have in like manner a similar set of positive currents flowing southwards. And, therefore, since positive currents flow out from the equator on both sides of it, we should have to contemplate a vertical stream of positive electricity at the equator which there splits itself up into two portions—one for each hemisphere.

The argument as I have now advanced it is of a general nature and is twofold.

(1) In the first place it brings forward objections to the localization of the cause of the diurnal variations anywhere else than in the higher regions of the Earth's atmosphere; then points out that if this cause exist in these regions it must be in the shape of a system of electric currents; and finally endeavours to show that there are no valid objections to such a system of currents.

(2) It endeavours to show that, if we take the diurnal

variation of the declination-needle, which is of a remarkably simple type, we have great difficulty in imagining that it can be brought about by any temporarily induced displacement of the magnetic system of the earth, while we can with the greatest ease account for it by means of a system of currents in the upper regions of the Earth's atmosphere.

At this point Dr. Schuster has endeavoured to apply mathematical analysis to the subject, and he has obtained results which are very satisfactory and encouraging *. He had previously, in the Report of the Magnetic Committee of the British Association for the year 1885, pointed out the existence of a test † which will enable us to decide whether or not the diurnal variation can be caused by a series of electric currents which embrace both the upper atmospheric regions and the Earth, and complete themselves by electric discharges through the lower regions of the Earth's atmosphere into the ground; and he now endeavoured to ascertain whether the supposed vertical currents at the equator, to which allusion has been made, could possibly be of this nature. If this were the case, he argues, and if a unit pole were carried from a position A at the Earth's surface in a path which should return again to A, and in the centre of which there should exist such a vertical current, then through all its course work would be done either by or against this pole, inasmuch as there would be a continued effort of the vertical current to turn the pole round it in one direction. In other words, the pole and the point A being immersed in the system of currents, there would be a potential having multiple values. On the other hand, if the system which produces the daily variation be outside of A, whether above or below it, there will be at A a true potential, and if the unit pole be carried as before, in any path from A and back to A again, as much work will be done against the pole as will be done by it. Let us consider, now, a little path embraced between two parallels of latitude near each other, and two meridians of longitude likewise near each other, and imagine our pole to be carried round this boundary. On the

* Proc. Lit. & Phil. Society of Manchester, January 12, 1886; Phil. Mag. April 1886, p. 349.

† The reader will find a complete discussion of this subject in Maxwell's 'Electricity and Magnetism.'

supposition that there is no vertical current in the centre of the path, the work done upon the pole will be equal to that done by it. This will at once give us an equation between X and Y; that is to say, between the components of the solar-diurnal periodic force towards the geographical north and west respectively. From this equation, and by means of certain legitimate assumptions regarding the type of Y, which represents very nearly the force influencing the declination (and this we know to be of a simple uniform type), Dr. Schuster is able to obtain certain relations between the solar-diurnal variations of the declination and of the horizontal force which ought to hold, *if there be no vertical currents between the upper regions and the Earth*, or, rather, if such vertical currents are inoperative as an element in producing the solar-diurnal variation. One of these is that the northerly or horizontal-force component of the daily variation ought to have a maximum or a minimum at the time when the westerly or declination component vanishes, that is to say attains its mean position.

Now at Greenwich, X or the horizontal-force component has a maximum at 7 o'clock in the evening and a minimum at noon; while Y or the declination component vanishes a little after 7 o'clock and between 12 and 1 in the afternoon. At Bombay the declination-needle is at its mean value on an average a little after 10 in the morning and about 10 in the evening. The horizontal force has its maximum a little after 11 in the morning and the minimum at a quarter past 9 in the evening.

The observations at Lisbon and Hobarton show an equally good agreement, those at St. Helena and the Cape of Good Hope less so; but in these two latter places the observations taken at different months show a considerable difference of behaviour. On the whole, Dr. Schuster regards the agreement as satisfactory, and as so far tending to disprove the existence of vertical currents through the Earth's surface. Pursuing his analysis, he comes to the conclusion, from certain approximate expressions which he obtains, that the northerly force ought to be a maximum in the morning and a minimum in the afternoon in the equatorial regions; while in latitudes above 45° the minimum ought to take place in the morning.

Now this is almost exactly what happens. At Bombay, for instance, the *maximum* of horizontal force takes place at 11 A.M., while at Greenwich the *minimum* takes place a little after that time.

Having thus obtained results which lead him to infer that the unit pole we are observing is not immersed in the attracting system, Dr. Schuster next proceeds to discuss the question whether this system is above us or beneath us. To do this it is necessary first of all to obtain an approximate value for the potential at the surface of the earth, and from it to derive the general potential. To aid in determining this we must bear in mind that, since the unit pole is now assumed not to be immersed in the attracting system, the potential V will be subject to the condition

$$\frac{d^2V}{dx^2}+\frac{d^2V}{dy^2}+\frac{d^2V}{dz^2}=0$$

or to an equivalent condition adapted to the system of coordinates employed. From this Dr. Schuster deduces two possible expressions for the potential; the one referring to a system above our heads and having powers of (r) the radius in its numerator, the other referring to a system beneath our feet and having powers of the radius in its denominator. Now the expression for the vertical force as derived from the potential will be $-\frac{dV}{dr}$, the sign of which will be manifestly different according as r appears in the numerator or in the denominator of the potential in question. Which, therefore, of these two possible (approximate) forms of V agrees best with observation? In the first place, both expressions found by Dr. Schuster have their turning-points coincident in epoch with those for X, or the northerly component of the disturbing force; and this is a fact confirmed by actual observation. But while the expression for the vertical force derived from a system above us has its maxima and minima coincident with those of horizontal force at latitudes greater than 45°, in the equatorial regions the maximum of horizontal force ought to be coincident with the minimum of vertical force, and *vice versâ*. Precisely the opposite arrangement should hold if the attracting system be beneath our feet.

Now at Greenwich the maximum of northerly force takes place at 7 P.M. and the minimum at noon; while the maximum of vertical force takes place at 7 P.M. and the minimum at 11 A.M.

At Bombay the maximum of northerly force takes place at 11 A.M. and the minimum at 9 P.M.; there is a very decided minimum of vertical force at 11 A.M., but there is no pronounced maximum; two minor maxima, however, occur, one at 6 A.M. and the other at midnight.

On the whole it must be said that the results of this first and praiseworthy attempt are very encouraging, and point to the supposition that the greater portion of the disturbing currents lies outside the Earth's surface.

I now come to consider another aspect of the subject. It seems quite possible to conceive a set of currents to exist in the Earth's atmosphere without exhibiting a considerable diurnal variation. Let us take, for instance, an ordinary electric circuit, say of a circular shape and horizontal, and heat it by causing some source of heat, such as a lamp, to travel slowly around it with a definite rate of progress. It will be evident that we shall have (assuming the current to be otherwise constant) no variation in flow due to this heating effect. In like manner, if there be electric currents in the atmosphere which circulate round the Earth in the direction of parallels of latitude, such currents will not be subject to a considerable solar diurnal variation. For while the conductivity of a given region would vary according to the position of the Sun with regard to it, yet the whole circuit round the Earth, which would always embrace a region affected by the Sun, would not have its total resistance altered, at least not greatly altered; and as there would be no cause for much alteration of the total electromotive force, there would be no great reason for inconstancy of current—in other words, no great solar diurnal variation.

It may, however, be asked if there are any grounds for imagining the existence of such a set of currents. To this I would reply that, assuming the existence of currents in the upper regions of the atmosphere, their disposition would certainly be to some extent subject to magneto-electric considerations. If we bear in mind the distinct connection between

auroral beams and lines of magnetic force, we must certainly, I think, be prepared to admit the possibility of perhaps even a marked reference to magneto-electric considerations in the disposition of the currents in question.

For the purpose of the following argument we may consider the Earth to be at rest (*i. e.* devoid of rotation), and imagine that the Sun circulates round the equator in twenty-four hours. As a consequence of solar influence, we shall have convection-currents in the upper regions of the atmosphere flowing from the equator northwards and southwards towards the poles. Whether these currents reach the poles or come down in some intermediate region may be left an open question. Now such currents will not only be conductors, but they will form a movable system of conductors, which we may suppose to be created at the equator when they rise into the upper regions, and destroyed at the poles or those intermediate regions where they descend.

Again, for the purpose of this argument we may, without sensible error, look upon the magnetic Earth as similar to the class model that is sometimes used to represent it; that is to say, as a globe wrapped round continuously with insulated wires in the same direction which convey an electric current, the circles of such wires being small near the poles, and of course large at the equator. Now if an external insulated circuit of wire a trifle larger than the diameter of this globe be supposed to travel from the equator to either of the poles, it will leave behind more convolutions of the primary globe-current than it approaches, and will therefore be traversed by an induced current in the same direction as that of the primary; and the continuous travelling of such an external insulated system might be supposed to increase the magnetic power of the globe. Applying the same sort of reasoning to the Earth and to the convection-currents under consideration, these may be imagined to be traversed by equatorial currents, the tendency of which in both hemispheres would be to increase the general magnetism of the globe. From the reason already given such currents would have no solar-diurnal variation, but yet they would be dependent upon the state of the Sun and would vary with it. For imagine a change to take place in the radiation of our luminary producing an excess of such rays as are greedily absorbed by the upper

atmospheric regions; there would be (as I have before remarked) a sensible increase in the conductivity of these regions even if the electromotive force remained altered, and hence there would be an increase in the supposed equatorial current. In other words, such currents, while presenting no great diurnal variation, due to the carriage of a constant Sun round the Earth, would yet be eminently susceptible to any inconstancy in the sun itself. Now have we any such phenomenon connected with terrestrial magnetism? I think we have. The late John Allan Broun has, I believe, proved that we have changes in the mean daily value of the horizontal force which are simultaneous, and in the same direction at places on the Earth's surface very far removed from each other; and I have endeavoured to show that the changes of this nature recorded by him depend, as far as we can judge from somewhat imperfect records, upon the state of the Sun's surface, an increased area of spotted surface coinciding apparently with increased values of the daily means of horizontal force all over the Earth. But my chief object in giving prominence to this part of the subject is with the view of advocating that the Gaussian method of analysis should not be applied merely to the solar diurnal variations of the three magnetic elements, but that they should likewise embrace a consideration of the simultaneous variations in the mean daily values of the elements at various stations. We must, in fine, consider the possibility at least of there being in the upper atmospheric regions, not merely currents which present a solar-diurnal variation, but others that have no such variation, while yet they may be highly susceptible to changes in the Sun. The double method of treating mathematically not merely the solar-diurnal variation, but likewise the simultaneous changes in the mean daily values of the elements, would thus appear to be necessary, and sufficient for giving us the required information. Already the Greenwich scheme of publication embraces not merely information connected with the solar-diurnal variation, but gives us likewise the mean daily values of the three elements; and if a complete system of this nature be pursued by a sufficient number of well-equipped magnetical observatories, we may hope soon to obtain reasonably complete information regarding the existence and distribution of currents in the upper regions of the Earth's atmosphere.

VII. *On a Modification of* Wheatstone's *Rheostat*. *By* SHELFORD BIDWELL, *M.A.**

IT is frequently desirable that the resistance of a circuit through which a current of electricity is flowing should be made to vary *continuously* and not by steps, as is necessarily the case when resistance-coils are used alone. An instrument for effecting this object was devised by Sir Charles Wheatstone in 1843, and was called by him the Rheostat. Two forms of the apparatus, both of which are well known, are described in his paper on the "Constants of the Voltaic Circuit," originally published in the Phil. Trans., and contained in the Physical Society's Reprint of Wheatstone's Scientific Memoirs.

In the first form two equal cylinders, one of wood and the other of brass, are mounted on parallel axes, and so arranged that a fine wire can be wound off the one and on to the other by turning a handle. On the wood cylinder a spiral groove is cut in which the wire lies, so that its successive convolutions are insulated from each other; but when any portion of the wire is wound upon the brass cylinder, the current passes immediately from the wire to the cylinder, and thence to one of the terminals of the instrument. The effective part of the length of the wire is therefore the variable portion which is on the wood cylinder.

In the other form there is only one cylinder, which is of wood, and has a quantity of stout wire permanently wound upon it in a spiral groove cut upon its surface. Near the cylinder and parallel to its axis is a brass rod, upon which a notched "rider," or in more modern instruments a grooved brass wheel, is capable of sliding. The notch in the rider, or the groove in the wheel, fits and presses upon the spiral wire, and when the cylinder is turned the rider or wheel moves longitudinally along the brass rod. The terminals of the instrument are connected respectively with the brass rod and with one end of the wire upon the cylinder; and the resistance introduced into the circuit depends upon the position of the point of contact of the rider or wheel with the wire.

The apparatus in either form is open to serious practical

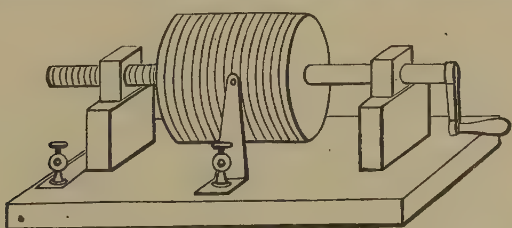
* Read May 8, 1886.

objections. In that first described it is difficult to maintain good electrical contact between the wire and the brass cylinder, both of which must be kept perfectly clean and free from dust and damp. Moreover the wire is liable to become slack and to leave its groove, and not unfrequently it breaks. In the second form there is also a difficulty in securing uniformly good contact; and if the slider fits the rod sufficiently tight, the lateral pressure upon the wire is so great that it becomes permanently stretched, and is sometimes forced completely out of its groove. The wire, too, is necessarily thick; and the whole apparatus must consequently be large and cumbersome if it is to work through any considerable range of resistance.

A Wheatstone's rheostat in good working order is rarely seen, even in the shop of the instrument maker; and in point of fact it is little used except for the purpose of lecture-illustration.

In the course of some experimental work the pressing need of some means of continuously varying a resistance led me to devise the modified rheostat, which is figured in the annexed woodcut.

As in the second form of Wheatstone's instrument, a wire is coiled in a spiral groove upon an insulating cylinder. This is mounted upon the middle of a brass axle of rather more than three times its length. Upon one of the projecting ends of the axle a screw is cut, the pitch of which is equal to



the distance between the consecutive turns of the wire. The axle revolves in two brass bearings, fixed at a distance apart equal to twice the length of the cylinder; one of the bearings has an inside screw corresponding with that upon the axle. A flat spring is attached at one end to the base-board of the instrument midway between the bearings; to the other end is riveted a short copper pin, which is directed perpen-

dicularly to the axis of the cylinder and bears upon the spiral wire, being kept in position by a shallow notch cut in its end. One end of the spiral wire is electrically connected with the brass axle, and thence through the screwed bearing and a strip of copper with a terminal upon the base-board. The spring is directly connected with a second terminal. When the cylinder is turned by means of a handle, it travels backwards or forwards in the direction of its axis, the point of contact of the copper pin with the spiral wire remaining fixed in space ; thus more or less resistance is introduced between the axle and the spring, and therefore between the two terminals.

In the model exhibited at the meeting of the Physical Society, the length of the cylinder is 3 cm., its diameter is 8 cm., and the diameter of the wire, which is of German silver, is 0·5 mm. There are nine turns of wire per centimetre of length, and the greatest resistance is about 10 ohms. Since the instrument is generally used in conjunction with a set of coils, this resistance is for most purposes amply sufficient ; indeed I am inclined to think that it would be on the whole advantageous to use thicker wire and wind it in a coarser spiral, so that the total resistance might be slightly more than one ohm. The rheostat would then be used merely as a fine adjustment*.

The advantages which this apparatus appears to possess over the usual forms are obvious. It is simple, compact, easily made, and not easily put out of order. There is no lateral stress, and in consequence of the rubbing action the contact is always good. The deflections of the needle of a "dead-beat" galvanometer in circuit with it are under perfect control, responding to the rotation of the cylinder with smoothness and regularity, and there is complete freedom from jerks and retrograde movements. It is not indeed

* The best form of cylinder would, I think, be a hollow brass drum covered with a tightly fitting tube of ebonite, 2 or 3 mm. in thickness. Wood, even when well seasoned, is liable to shrink, and is more or less affected by moisture. The depth of the groove should be about half the diameter of the wire. The wire should be annealed, and should be wound on when it is warm. The notch at the end of the copper pin may be very shallow, for if the position of the spring is properly adjusted the pin has little or no tendency to slip off the wire.

more suitable for use as a measuring instrument than the older forms; but when it is desired to adjust a resistance to a nicety, or to cause a continuous variation of a current, it is of great utility. If the interposed resistance is required to be known with accuracy, it should be measured by the bridge-method in the ordinary way.

VIII. *On a Theorem relating to Curved Diffraction-gratings.* *By* WALTER BAILY, *M.A.**

IN a paper read before this Society in January 1883 †, I showed that if a plane be taken perpendicular to the lines of a curved diffraction-grating, and the normal to the centre of the grating be taken as the initial line, then the equation

$$\frac{\cos^2\theta}{r}=\frac{\cos\theta}{c}+\frac{1}{d}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which c is the radius of curvature of the grating and d is an arbitrary constant, gives a curve having the property that if a source of light is placed at any point of the curve, the curve is the locus of the foci of all diffracted rays whether reflected or transmitted.

When d is greater than c, r may be infinite. Let ϕ be the value of θ for which r is infinite. Then

$$0=\frac{\cos\phi}{c}+\frac{1}{d},$$

and the equation to the curve may be written

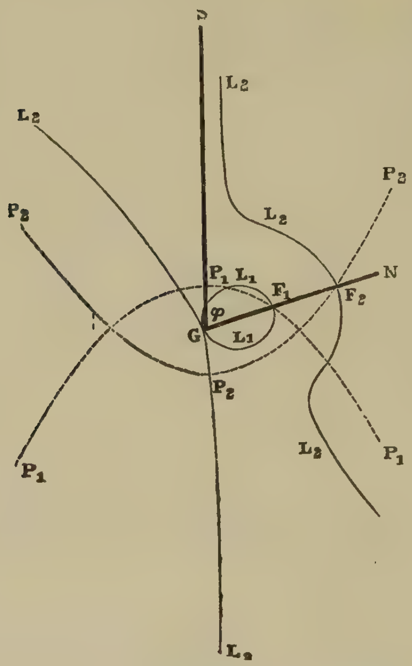
$$\frac{c}{r}\cdot\cos^2\theta=\cos\theta-\cos\phi. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In fig. 1, G is the diffraction-grating and G N its normal; and the angle N G S is equal to ϕ. The curves marked L_1, L_2 are traced from equation (2). G S is parallel to one asymptote to the curve, so that if a source of light (say a star) is at an infinite distance on the corresponding branch of the curve it lies in the direction G S; and the foci of its diffracted light

* Read May 8, 1886.
† Proceedings, vol. v. p. 181.

lie on the curves L_1, L_2. The foci of reflected light will lie on

Fig. 1.



the oval marked L_1, and the foci of transmitted light will lie on the branches marked L_2.

Let F_1, F_2 be the points at which these curves cut the normal to the grating, and let $GF_1=\rho_1$ and $GF_2=\rho_2$. The points F_1, F_2 I will call the normal foci; F_1 is the normal focus for reflected light, and F_2 for transmitted light.

Putting $r=\rho_1$ and $\theta=0$ in (2), we have

$$c/\rho_1=1-\cos\phi; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and, again, putting $-r=\rho_2$ and $\theta=\pi$, we have

$$c/\rho_2=1+\cos\phi. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Now suppose G S the direction of the star to be kept fixed, and the grating turned so as to vary the value of ϕ; then

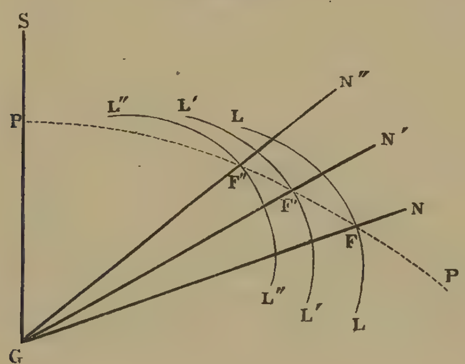
equations (3) and (4) will give the loci of F_1 and F_2 respectively. The loci are the parabolas marked P_1 and P_2. They have a common focus G, and common axis GS, and a common latus rectum $=2c$.

F_1 is the real focus of reflected light, having a wave-length $=\frac{\sigma}{n}\sin\phi$, where σ is the distance between the lines of the grating, and n is an integer.

F_2 is the virtual focus of transmitted light having the same wave-length.

In fig. 2, P P is part of the parabola (on a larger scale)

Fig. 2.



which is the locus of the normal focus of reflected light; G N, G N′, G N″ are difference positions of the normal to the grating; and L L, L′ L′, L″ L″ are respective positions of the spectra, and F, F′, F″ are respective positions of the normal foci.

The theorem is, When the source of light is at an infinite distance the normal foci lie on two parabolas whose common focus is the centre of the grating and common latus rectum is equal to the diameter of curvature of the grating; the parabolas for reflected light being convex to the source of light, and those for transmitted light being concave.

IX. *Some Thermodynamical Relations.*—PART IV.

By WILLIAM RAMSAY, *Ph.D., and* SYDNEY YOUNG, *D.Sc.**

SINCE the first portions of this research were published Professors Ayrton and Perry have criticised our work, and while we would thank them for the appreciative way in which they speak of our labours, we must differ entirely from their conclusion that "there is nothing further to be said about the four laws in question." This conclusion rests on a complete misapprehension of the whole scope of our papers, and for the obvious reason that, while we have endeavoured by a method of what may be termed approximation to arrive at a workable plan of deducing from the known vapour-pressures of a substance like water the unknown vapour-pressures of any other substance with as little expenditure of experimental work as possible, and have in our research made the statement, which is only a very rough approximation to truth, that the ratios of the absolute temperatures of any two liquids at any given pressure are equal to the ratios at any other pressure, but have materially modified this statement, and asserted next, what is a very close approximation to truth, that when the statement given does not hold (as in by far the majority of cases), the relation of the ratios is expressed by the equation

$$R' = R + c(t' - t)$$

(where R' is the ratio of the absolute temperatures of any two bodies at a given pressure ; R the ratio at another pressure ; t and t' the temperatures of one of the two bodies corresponding to those vapour-pressures ; and c is a constant). Professors Ayrton and Perry have based all their reasoning on the first statement, which laid no claim to exactitude, and have informed us, what we already knew, that Dalton's law gives better results. The data given in our previous papers, however, show how nearly our generalization agrees with fact.

To refute the accusation of having performed useless labour would be really to repeat the substance of our previous papers; but the members of the Physical Society would hardly thank

* Read May 8, 1886.

us were we to do so. There are, however, two or three remarks made by our critics which call for special reply.

1. It is suggested that our obvious course would have been to employ Rankine's formula, which, our critics state, is not empirical, but based on Rankine's molecular theory. We have been informed that the formula deduced by Rankine from his molecular theory was found by him not to agree with the experimental results; and that, in order to secure agreement, an empirical term was added. We would ask if this was not the case, and, if so, whether the whole formula is not thereby rendered empirical?

2. We are told that our labours might have been reduced by 75 per cent. had we recognized the fact that our four laws are identical. Now we do not anywhere state that our "laws" are absolute, in which case only would the identity necessarily hold; but indeed give methods for calculating their deviation from constancy. It is moreover desirable to test the truth of such statements in every possible way, inasmuch as different determinations by different observers are thereby introduced.

3. That it is by no means impossible to obtain with accuracy the specific volumes of saturated vapour will appear from memoirs on the thermal behaviour of ethyl alcohol and ether, which are in the hands of the Royal Society; indeed such measurements can be made at temperatures when a direct determination of L would be extremely difficult, if not impossible. To show the necessity of using determinations from all sources, we may point out that if Regnault's values of L and of $\frac{dp}{dt}$ for alcohol and for ether are employed, and the vapour-density calculated by the thermodynamic equation

$$\frac{\mathrm{L}}{s_1-s_2}=\frac{dp}{dt}\cdot\frac{t}{\mathrm{J}},$$

impossible values are obtained, unless it is supposed that chemical dissociation takes place, which is absurd.

4. We are told that the equation numbered (6) (p. 371 of the 'Proceedings'), $t=a\psi(p)$, is identical with our four "laws;" and that "if (6) is true, then it follows that the ratio of the absolute temperatures of two vapours to one another at

any pressure is the same as at any other pressure, or $\theta = \kappa t$ (7). In fact, then, we can test laws I., II., III., and IV. by simply testing (7); and as we find from Regnault and Rankine's formula that (7) is untrue, there is nothing further to be said about the four laws in question." We hope that no one has, like Professors Ayrton and Perry, so misunderstood our papers as to suppose that we imagine that "the ratio of the temperatures of two vapours at any pressure is always the same as at any other pressure." We do, indeed, notice that this statement holds with very close approximation for like bodies, such as chloro- and bromo-benzene; but the whole of the second and third parts of our memoir are devoted to an attempt, which we deem not unsuccessful, to give a method whereby the *deviation from the above statement can be estimated.*

The didactic remarks so kindly directed to us at the beginning of Messrs. Ayrton and Perry's critique, lead us to suppose that the great importance of such problems in Chemistry is not so generally known as we had imagined; and we would cordially agree that the cooperative principle may here with advantage be applied, and physicist and chemist mutually assist each other.

The problem of dissociation has for long invited the attention of chemists. Many compounds decompose at a moderately high temperature, and their constituents reunite when the temperature is lowered. It is argued that, were it possible to attain a sufficiently high temperature, all the simpler compounds at least would exhibit the phenomena of dissociation.

From the nature of gases, it is to be expected that a study of the behaviour of dissociating gases would be the simplest way of arriving at a knowledge of the subject. An obvious criterion of the amount of dissociation is given by the vapour-density of the partially dissociated body; for if the dissociating gas, and the simpler gases resulting from its dissociation, obey Boyle's and Gay-Lussac's laws, then it is easy to calculate from the density of the gas the percentage number of molecules decomposed. But there is no means of knowing whether the dissociating substance, as such, does or does not obey these laws; hence it is evidently desirable to ascertain the behaviour of substances which do not dissociate as regards

expansion and compressibility; so that some idea may be gained as to the influence exerted by molecular attraction between like molecules on the volume they occupy. An investigation of this nature is best carried out by ascertaining the behaviour of gases when they are becoming increasingly subject to molecular attraction, *i. e.* when they are approaching the condition of saturated vapours. The pressure of saturation is, under normal circumstances, identical with the vapour-pressure; hence the importance of a knowledge of this quantity. We have before remarked, that we have communicated to the Royal Society the results of experiments on alcohol and ether with this view.

Again, if the body exerting vapour-pressure be one capable of partial dissociation on passage from the solid or liquid to the gaseous state, its apparent vapour-pressure will really consist of its real vapour-pressure, and also of the pressure due to its dissociation into its constituents. It is evidently of importance to determine the latter independently of the former; and it is only by the employment of some law applicable to all bodies, and deduced from the behaviour of stable substances, that an idea can be formed of the pressure due to the second cause.

In the Philosophical Magazine for April 1886, p. 299 (*ante*, p. 22), Professor Unwin also comments on our papers, and, unlike Professors Ayrton and Perry, has appreciated our motive in bringing forward the subject. We have to thank him for pointing out the relation of the ratio of the total heat of vaporization to the heat expended in external work, deduced from the second half of the thermodynamic equation. We agree with him that the approximate constancy there observed lies at the basis of all the relations found by us.

We have taken the liberty of applying his formula

$$\frac{t^{n+1}}{p} \times \frac{dp}{dt}$$

to alcohol, ether, and mercury, using the vapour-pressures determined by us over a wide range of temperatures in the first two cases; and for mercury, the results given in the Journ. Chem. Soc. 1886, p. 37.

We have taken the value of $(n+1)$ for alcohol as 2·248, for ether as 2·23, and for mercury as 2·21.

The values of the expression $\frac{t^{n+1}}{p} \cdot \frac{dp}{dt}$ at different pressures are as follows:—

Alcohol.				Ether.			
Press. millim.	Temp. abs.	$\frac{dp}{dt}$.	$\frac{t^{2 \cdot 248}}{p} \cdot \frac{dp}{dt}$.	Press. millim.	Temp. abs.	$\frac{dp}{dt}$.	$\frac{t^{2 \cdot 23}}{p} \cdot \frac{dp}{dt}$.
23·733	283	1·516	20700	184·9	273	8·843	12950
540·91	343	22·750	20376	921·18	313	31·16	12393
1692·3	373	58·175	20721	2293·9	343	62·84	12341
2359·8	383	75·95	20592	7495·7	393	153·95	12156
5686·6	413	151·75	20226	13281	423	234·9	12715
14764	453	315·45	19931	21804	453	336·4	12921
22182	473	430·8	19966				
45519	513	763·7	20703				

Mercury.

Pressures, millim.	Temp. abs.	$\frac{dp}{dt}$.	$\frac{t^{2 \cdot 21}}{dt} \cdot \frac{dp}{dt}$.
10·0	457·30	0·350	26486
100·0	534·20	2·506	26743
200·0	563·44	4·470	26833
500·0	608·03	9·40	26703
1000·0	647·20	16·37	26697
3000·0	723·10	38·61	26811
5000·0	765·60	56·90	26904

With mercury, the value of n is much more nearly constant than if Regnault's numbers be employed.

It will be noticed that this number is much higher than that given by Professor Unwin (0·69, while ours is 1·21); but it is worthy of remark, that if the values of n be calculated for the stable substances mentioned in our first paper, taking the highest and lowest pressures, and the corresponding values of $\frac{dp}{dt}$, the value of n varies between the narrow limits 1·15 and 1·52. Although we have not verified these values for intermediate pressures except in the examples already given, it may be of interest to reproduce them.

Substance.	Pressures from which n was calculated.	Value of n.
Carbon disulphide	50 and 5000	1·147
Ethyl bromide	50 and 5000	1·316
Ethyl chloride	50 and 5000	1·243
Carbon tetrachloride . .	50 and 5000	1·326
Bromobenzene	50 and 800	1·475
Chlorobenzene	100 and 700	1·480
Chloroform	200 and 5000	1·376
Ethylene	10 and 400	1·235
Sulphur	300 and 3000	1·251
Bromo-naphthalene . . .	150 and 800	1·196
Methyl salicylate	50 and 800	1·517
Aniline	50 and 800	1·218
Methyl alcohol	50 and 5000	1·395

It was found impossible to obtain a constant value for n with dissociating substances when different pressures were employed.

The whole subject of vapour-pressure is one that cannot well be considered on its own merits, for they must evidently be intimately related to other physical properties; and although we have already accumulated data for alcohol and ether bearing on this subject, we prefer to reserve a general consideration of the question until an investigation, as regards the thermal behaviour of other bodies, on which we are at present engaged, shall have been finished.

X. *Some Thermodynamical Relations.*—Part V.

By William Ramsay, *Ph.D.*, *and* Sydney Young, *D.Sc.**

In the first two of the series of papers on "Some Thermodynamical Relations," published in the previous volume of the 'Proceedings' (vol. vii.), it was shown by one of us that the ratio of the absolute temperatures of nearly related bodies, such as chlorobenzene and bromobenzene, or ethyl chloride and ethyl bromide, is constant for equal vapour-pressures; and that a relation exists between the ratios of the absolute temperatures of all bodies which may be expressed

* Read May 22, 1886.

by the equation

$$R' = R + c(t' - t),$$

where R is the ratio of the absolute temperatures of the two bodies corresponding to any vapour-pressure, the same for both; R′ is the ratio at any other vapour-pressure, again the same for both; c is a constant which may be 0 or a small + or − number; and t' and t are the temperatures of one of the two bodies corresponding to the two vapour-pressures.

The determination of the vapour-pressures of a large series of compound ethers by Schumann (Wiedemann's *Annalen*, 1881, p. 40) affords an opportunity of studying the relations of a great number of bodies of the same type; and it appears that in this case also the ratio of the absolute temperatures of any two of the ethers is a constant at all pressures. The following table shows the ratios of the absolute temperatures of all the ethers

Ratios of Absolute Temperatures of Ethers to those of Ethyl Acetate at definite Pressures.

Ether.	Pressure.			Mean.
	1300 millim.	760 millim.	200 millim.	
Methyl formate	·8715	·8720	·8706	·8714
Ethyl formate	·9344	·9352	·9323	·9340
Propyl formate	1·0109	1·0111	1·0115	1·0112
Isobutyl formate	1·0585	1·0594	1·0573	1·0584
Amyl formate	1·1345	1·1320	1·1329	1·1331
Methyl acetate	·9420	·9440	·9431	1·9430
Propyl acetate	1·0678	1·0677	1·0690	1·0682
Isobutyl acetate	1·1122	1·1120	1·1120	1·1121
Methyl propionate	1·0073	1·0080	1·0073	1·0075
Ethyl propionate	1·0615	1·0605	1·0614	1·0611
Propyl propionate	1·1290	1·1288	1·1291	1·1290
Isobutyl propionate	1·1704	1·1705	1·1705	1·1705
Amyl propionate	1·2366	1·2374	1·2401	1·2380
Methyl butyrate	1·0724	1·0720	1·0716	1·0720
Ethyl butyrate	1·1220	1·1223	1·1202	1·1215
Propyl butyrate	1·1889	1·1874	1·1902	1·1888
Isobutyl butyrate	1·2279	1·2279	1·2278	1·2279
Amyl butyrate	1·2905	1·2899	1·2901	1·2902
Methyl isobutyrate	1·0444	1·0434	1·0433	1·0437
Ethyl isobutyrate	1·0953	1·0943	1·0935	1·0944
Propyl isobutyrate	1·1604	1·1623	1·1609	1·1612
Isobutyl isobutyrate	1·2001	1·1985	1·1985	1·1990
Amyl isobutyrate	1·2644	1·2619	1·2637	1·2633
Methyl valerate	1·1135	1·1131	1·1139	1·1135
Ethyl valerate	1·1642	1·1634	1·1619	1·1632
Propyl valerate	1·2257	1·2251	1·2265	1·2258
Isobutyl valerate	1·2635	1·2617	1·2634	1·2629

to those of ethyl acetate at pressures of 200, 760, and 1300 millims. (The boiling-points at these pressures are given by Schumann.) It will be seen that in every case the ratio is very nearly constant at each pressure; and the deviations from constancy may well be due to the great difficulty of obtaining perfectly pure specimens, evidenced by the fact that only one ether boiled with perfect constancy, the rise of temperature during distillation amounting in one case to 0°·7, while the average rise was 0°·37. The absolute temperatures of ethyl acetate corresponding to 1300, 760, and 200 millim. are 367°·3, 350°·1, and 314°·4.

Taking the mean ratio for each ether, and the temperatures of ethyl acetate at the three pressures as correct, the boiling-point of the ethers were recalculated; and the following table contains these values, together with the observed temperatures and the differences between the observed and calculated temperatures :—

Absolute Temperatures.

Ether.	Observed.			Calculated.			Differences.		
	1300 mm.	760 mm.	200 mm.	1300 mm.	760 mm.	200 mm.	1300 mm.	760 mm.	200 mm.
Methyl formate......	320·1	305·3	273·7	320·1	305·1	274·0	0	−0·2	+0·3
Ethyl formate	343·2	327·4	293·1	343·1	327·0	293·6	−0·1	−0·4	+0·5
Propyl formate	371·3	354·0	318·0	371·4	354·0	317·9	+0·1	0	−0·1
Isobutyl formate ...	388·8	370·9	332·4	388·7	370·5	332·8	−0·1	−0·4	+0·4
Amyl formate	416·7	396·3	356·2	416·2	396·7	356·2	−0·5	+0·4	0
Methyl acetate	346·0	330·5	296·5	346·4	330·0	296·5	+0·4	−0·5	0
Propyl acetate	392·2	373·8	336·1	392·3	374·0	335·8	+0·1	+0·2	−0·3
Isobutyl acetate ...	408·5	389·3	349·6	408·5	389·3	349·6	0	0	0
Methyl propionate ..	370·0	352·9	316·7	370·1	352·7	316·8	+0·1	−0·2	+0·1
Ethyl propionate ...	389·9	371·3	333·7	389·7	371·5	333·6	−0·2	+0·2	−0·1
Propyl propionate...	414·7	395·2	355·0	414·7	395·3	355·0	0	+0·1	0
Isobutyl propionate	429·9	409·8	368·0	429·9	409·8	368·0	0	0	0
Amyl propionate ...	454·2	433·2	389·9	454·7	433·4	389·2	+0·5	+0·2	−0·7
Methyl butyrate ...	393·9	375·3	336·9	393·7	375·3	337·0	−0·2	0	+0·1
Ethyl butyrate	412·1	392·9	352·2	411·9	392·6	352·6	−0·2	−0·3	+0·4
Propyl butyrate ...	436·7	415·7	374·2	436·6	416·2	373·8	−0·1	+0·5	−0·4
Isobutyl butyrate ...	451·0	429·9	386·0	451·0	429·9	386·0	0	0	0
Amyl butyrate	474·0	451·6	405·6	473·9	451·7	405·6	−0·1	+0·1	0
Methyl isobutyrate..	383·6	365·3	328·0	383·4	365·4	328·1	−0·2	+0·1	+0·1
Ethyl isobutyrate ...	402·3	383·1	344·1	402·0	383·2	344·1	−0·3	+0·1	0
Propyl isobutyrate ..	426·2	406·9	365·0	426·5	406·5	365·1	+0·3	−0·4	+0·1
Isobutyl isobutyrate	440·8	419·6	376·8	440·4	419·8	377·0	−0·4	+0·2	+0·2
Amyl isobutyrate ...	464·4	441·8	397·3	464·0	442·3	397·2	−0·4	+0·5	−0·1
Methyl valerate......	409·0	389·7	350·2	409·0	389·8	350·1	0	+0·1	−0·1
Ethyl valerate	427·6	407·3	365·3	427·2	407·2	365·7	--0·4	−0·1	+0·4
Propyl valerate......	450·2	428·9	385·6	450·2	429·2	385·4	0	+0·3	−0·2
Isobutyl valerate ...	464·1	441·7	397·2	463·9	442·1	397·1	0·2	+0·4	−0·1

It will be noticed that the greatest difference between the observed and recalculated temperatures is $0^\circ{\cdot}7$, which is probably within the limits of experimental error, for the reason already stated. If this is so, the equation $\frac{t_2'}{t_1'} = \frac{t_2}{t_1}$ holds good for this series of ethers, where t_2' and t_2 are the absolute temperatures of any one of the ethers corresponding to two vapour-pressures, and t_1' and t_1 the absolute temperatures of any other ether at the same pressures. If the ethers are compared with some other substance, such as water, the equation

$$\frac{t_1'}{\mathrm{T}'} = \frac{t_1}{\mathrm{T}} + c(\mathrm{T}' - \mathrm{T})$$

must be employed, where t_1' and t_1 are the absolute temperatures of the ether, and T′ and T those of water at any two pressures. If the left side of this equation be multiplied by $\frac{t_2'}{t_1'}$ and the right by $\frac{t_2}{t_1}$, $\frac{t_2'}{t_1'}$ being equal to $\frac{t_2}{t_1}$, the equation becomes

$$\frac{t_2'}{\mathrm{T}'} = \frac{t_2}{t_1}\left\{\frac{t_1}{\mathrm{T}} + c(\mathrm{T}' - \mathrm{T})\right\}$$

$$= \frac{t_2}{\mathrm{T}} + c\frac{t_2}{t_1}(\mathrm{T}' - \mathrm{T}).$$

That is to say, if the members of this series of ethers be compared with water, both the ratios at any given pressure, corresponding to t_1, t_2, &c. and the constant c vary directly as the boiling-points (absolute) of the ethers at that pressure.

Taking the boiling-point of ethyl acetate at the normal pressure to be correct, and the ratio of the absolute temperature of ethyl acetate to that of water at that pressure therefore to be $\frac{350{\cdot}1}{373{\cdot}0} = 0{\cdot}9386$, and the value of c to be $0{\cdot}000387$, the ratio of the absolute temperature of ethyl acetate to that of water at any other pressure is given by the equation

$$\frac{t'}{\mathrm{T}'} = 0{\cdot}9386 + 0{\cdot}000387\,(\mathrm{T}' - 373),$$

where t' is the absolute temperature of ethyl acetate, and T′ that of water.

The calculated and observed temperatures are :—

Pressure.	Temperature. Observed.	Temperature. Calculated.
1300	367·3	367·2
200	314·4	314·4

For any other ether in the series the equation is

$$\frac{t'}{T'} = \frac{t}{350 \cdot 1} \{0 \cdot 9386 + 0 \cdot 000387 \, (T' - 373)\},$$

where t is the boiling-point of the ether at constant pressure.

For pressures of 1300 and 200 millim. respectively the equation becomes simply

$$t' = 1 \cdot 0488 t$$

and

$$t' = 0 \cdot 89795 t.$$

It appears therefore that by determining simply the boiling-point of an ether belonging to this type, and knowing the vapour-pressures of water (or of one of the other ethers), it is possible to calculate the temperatures corresponding to any other pressure, at any rate between the limits of 200 and 1300 millim.